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ABSORPTION OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS OF 2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL

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RÉSUMÉ

Le dioxyde de carbone (CO_2) provenant de l'utilisation des combustibles fossiles est l'un des gaz à effet de serre le plus important. Dû à l'abondance et à la disponibilité des ressources en combustibles fossiles, il peut être envisagé qu'elles continueront de jouer un rôle important au niveau de l'économie énergétique mondiale. Le développement de nouvelles technologies pour l'absorption du CO_2 est donc crucial.

Les solubilités du CO_2 et du protoxyde d'azote (N_2O) dans les solutions aqueuses de 2-amino-2-hydroxyméthyle-1,3-propanediol (AHPD) ont été mesurées dans cette étude. La solubilité physique du CO_2 dans les solutions aqueuses de AHPD a aussi été estimée grâce à l'analogie du N_2O. Un modèle d'équilibre gaz-liquide a été développé afin de représenter la solubilité du CO_2 à l'équilibre dans les solutions aqueuses de AHPD. L'influence de l'enzyme anhydrase carbonique humaine sur la solubilité du CO_2 dans les solutions aqueuses de AHPD a aussi été étudiée.

ABSTRACT

Carbon dioxide (CO_2) from the use of fossil fuels resources is one of the most significant greenhouse gases. Due to the abundance and the availability of fossil fuels resources, it can be anticipated that they will continue to play a significant role in the world's energy economy. Therefore, the development of new technologies for the CO_2 absorption is crucial.

The solubilities of CO_2 and nitrous oxide (N_2O) in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) were measured in this study. The physical solubility of CO_2 in aqueous solutions of AHPD was also estimated by the N_2O analogy. A gas-liquid equilibrium model was developed to represent the solubility of CO_2 in aqueous solutions of AHPD at equilibrium. The influence of an enzyme, namely, human carbonic anhydrase on the solubility of CO_2 in aqueous solutions of AHPD was also studied.

FOREWORD

One chapter composes the present work. This chapter represents the core of a research article submitted to the scientific journal *Journal of Chemical and Engineering Data* at the time of this work deposit for evaluation (June 2007). This research article is named as follow:

The chapter is composed of this research article in its integrity. However, the figures and tables were displaced from the end of the research article to where they are mentioned in the text. The size of the figures and tables and the size of the characters inside of the figures were adjusted to fit with this paper. Three figures and two tables not presented in the research article were placed in the sections APPENDIX and are mentioned in the text. A discussion on the values presented in table B.1 is also placed in the text.

The research article was composed on my own and revised by Ion Iliuta, Maria Iliuta, Sylvie Fradette and Faïçal Larachi. Ion Iliuta worked for the development of the gas-liquid equilibrium model presented in the article. Maria Iliuta has already worked with the experimental system used in this research project and submitted two research articles before the beginning of my research project. She also did the initial set up of the experimental system used for my research project. Sylvie Fradette is a Ph.D. holder and works for a private company in Québec city, CO_2 Solution Inc., that is related to my research project. Faïçal Larachi is my research director.

Acknowledgments

Je dédie cet ouvrage à ma famille pour leur encouragement et leur support

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INTRODUCTION

I.1 Problem definition

Carbon dioxide (CO_2) is one of the most significant greenhouse gases due to the quantity of its emissions evaluated to be around 22 thousand millions tons/year from the use of fossil fuels alone. CO_2 emissions are currently supposed to be responsible for over 60 % of the enhanced greenhouse effect, methane (CH_4) emissions are supposed to contribute for 20% and the remaining 20% is caused by nitrous oxide (N_2O), a number of industrial gases and ozone [1]. Scientific evidence now strongly suggests that increased levels of greenhouse gases (GHG) may lead to higher temperature and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise by about 1.4-5.8 °C by the year 2100 [2]. Many consequences could be related to the enhancing greenhouse effect such as an increasing frequency of the extreme climate events, an important warming in some regions, disturbances in the precipitation cycle and increased sea levels.

Due to the availability of fossil fuel resources, it is anticipated that they will continue to play a significant role in the world's energy economy into this century. Moreover, CO_2 is also produced in large quantities by steel and cement production and from other industrial applications such as carbonation of brine, welding as an inert gas, food and beverage carbonation, dry ice, urea production and soda ash industry [1,3,4]. Industries seek ways to reduce their emissions but are constrained by the lack of practical technology and of clear governmental direction. Then, CO_2 absorption technology is of great importance nowadays for the prevention of global warming and the resulting worldwide climate change. Deployment of more efficient processes for the removal of CO_2 has become crucial, together with the development of new absorbents as one of the urgent areas of research in addressing global-warming problems. The CO_2 emissions from the industrial plants must be also reduced by improving the combustion processes.

Some technologies the capture of CO_2 and CO_2 sequestration have been developed and others are presently studied by different university or industrial groups. These technologies include the transformation of CO_2 by seaweeds, CO_2 sequestration in terrestrial reservoirs,

in deep seas, in soil and biomass, and carbon dioxide capture using chemical absorption processes [3]. Unfortunately, it must be mentioned that the environmental consequences of a large part of these techniques are still unknown or couldn't be demonstrated. Moreover, CO_2 sequestration in terrestrial reservoirs, in deep seas and in soil and biomass require the proximity of a large scale CO_2 emissions source from these sites. The transformation of CO_2 by seaweeds could be an interesting method for CO_2 capture and sequestration. It consists of using photosynthesis of seaweeds. Gas emissions from thermal power plants could be directly introduced in basins near the plant. The chosen seaweeds will have to support rigorous environmental conditions. The produced seaweeds could be dried and used as fuel to feed the plant. However, there is an important lack of knowledge about this technique and it could be complicated to establish on site.

Carbon dioxide capture using chemical absorption processes is one of the common industrial technologies today and has, in many cases, been found to be the most viable solution compared with other processes due to its low cost and simplicity [5-9]. The majority of these processes implicate the use of aqueous alkanolamine solutions. The use of these solutions has many advantages such as a higher purification of gases, less energy requirements and a higher CO_2 absorption capacity than the processes that use aqueous solutions of potassium carbonate.

The CO_2 absorption processes usually consist of circulating the gases through a column or a packed or trays column. The alkanolamine solution enters in the column by its upper part and the gases enter in the column by its bottom part. This technique is illustrated in Figure 1.1. It has been used for a long time and is still used in industries in gas-treating processes for the removal of CO_2 from gas streams in the natural gas, synthesis gases and synthetic ammonia industries, fossil-fuel power plants, coal gasification and petroleum chemical plants for operational, economical and environmental reasons [10,11]. Carbon dioxide present in natural gas will reduce the heating value of the gas, and as an acidic component, has the potential to cause corrosion in pipes and process equipment, and catalyst poisoning in ammonia synthesis [1,12]. This technique is also used for the removal of acid gases, like hydrogen sulphide (H_2S) and carbonyl sulphide (COS), since those are highly corrosive.
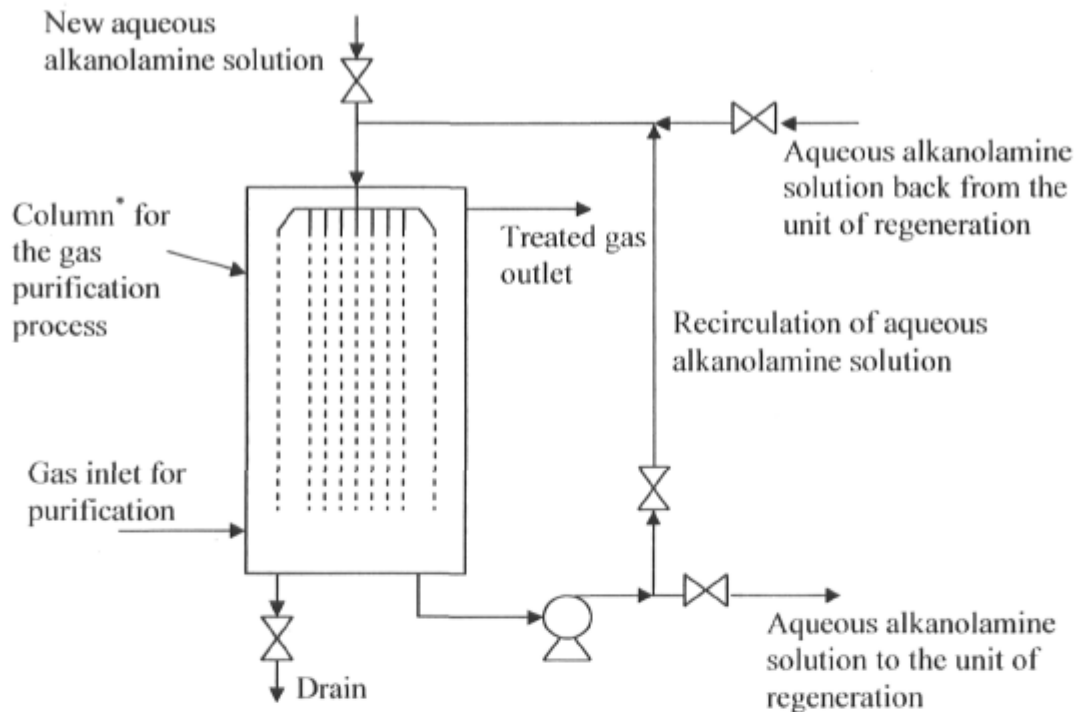
Figure I.1. Column for the gas purification process used to separate a gas mixture from its impurities such as acid gases (e.g., CO_2, H_2S, and SO_2) and organic sulfur compounds (e.g., COS, CS_2, mercaptans, and thiophene). * The column used for the gas purification process can also be a trays or packing column.

I.2 Chemical absorption mechanisms of carbon dioxide in aqueous alkanolamine solutions

I.2.1 Primary, secondary and tertiary amines

At this time, aqueous solutions of monoethanolamine (MEA)-[$HO(CH_2)_2NH_2$] are the most ubiquitous amine solutions used as absorbent for CO_2 capture using chemical absorption processes. Advantages of the use of aqueous solutions of MEA include their low molecular weight, high reactivity, low solvent cost, high absorbing capacity on a mass basis, reasonable thermal stability and thermal degradation rate, ease of reclamation and low absorption of hydrocarbons [1,13]. Aqueous solutions of diethanolamine (DEA)-[$(HO(CH_2)_2)_2NH$] and N-methyldiethanolamine (MDEA)-[$(HO(CH_2)_2)_2NCH_3$] are also widely used in industries as post-combustion CO_2 absorbent. MEA is a primary amine

(represented by RNH_2 where R is an alkyl radical), DEA is a secondary amine (represented by R_1R_2NH where R_1 and R_2 are alkyl radicals) and MDEA is a tertiary amine (represented by $R_1R_2R_3N$ where R_1, R_2 and R_3 are alkyl radicals).

The primary and secondary amines react with CO_2 to form species termed carbamates ($RNHCOO^-$ for a primary amine and $R_1R_2NCOO^-$ for a secondary amine) and protonated amines (RNH_3^+ for a primary amine and $R_1R_2NH_2^+$ for a secondary amine). It is assumed that the reaction takes place between a nonbonding electron pair at the amino nitrogen atom and an antibonding empty orbital in CO_2 for a donor-acceptor interaction. Several reaction mechanisms have been proposed in the literature [10,11,14-18]. One possibility is the following sequential reactions:

1. For primary amines:

$$CO_2 + RNH_2 \leftrightarrow RNHCOOH \tag{I.1}$$

$$RNHCOOH + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \tag{I.2}$$

2. For secondary amines:

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NCOOH \tag{I.3}$$

$$R_1R_2NCOOH + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{I.4}$$
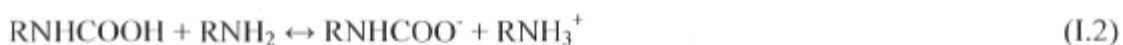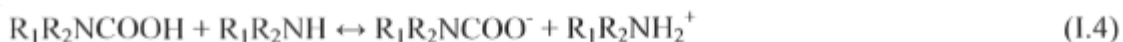
The first step, in which a carbamic acid ($RNHCOOH$ for a primary amine and R_1R_2NCOOH for a secondary amine) is formed, is bimolecular, of second order, and rate determining, while the second proton transfer step is assumed to be rapid. It has also been proposed that carbamate formation may take place via a mechanism involving a zwitterion intermediate in the following way [10,11,14,16-18]:

1. For primary amines:

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+CO_2^- \tag{I.5}$$

$$RNH_2^+CO_2^- + RNH_2 \leftrightarrow RNHCO_2^- + RNH_3^+ \tag{I.6}$$

2. For secondary amines:

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+CO_2^-$$ (I.7)

$$R_1R_2NH^+CO_2^- + R_1R_2NH \leftrightarrow R_1R_2NCO_2^- + R_1R_2NH_2^+$$ (I.8)
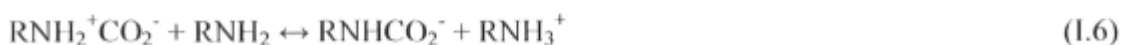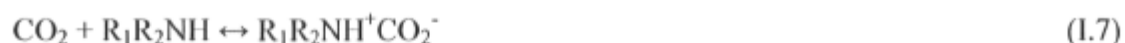
Again, the second step is an assumedly rapid deprotonation of the zwitterion ($RNH_2^+CO_2^-$ for a primary amine and $R_1R_2NH^+CO_2^-$ for a secondary amine). This mechanism has been a favored interpretation of experimental kinetic measurements [11,16,17,19,20] and has recently become one of the most widely accepted mechanism for primary and secondary amine reactions with CO_2 [6,14,18,21-24].

Another study [15] proposed an alternative termolecular mechanism that starts with a loosely bound encounter complex. A schematic drawing of this single step, concerted reaction mechanism is shown in Figure I.2. Bond formation between the nitrogen atom of alkanolamine with the carbon atom in CO_2 takes place with a simultaneous proton transfer from the amino nitrogen atom to a nearby base molecule. It is somewhat similar to the zwitterion mechanism described above, but it does not include any intermediate species.
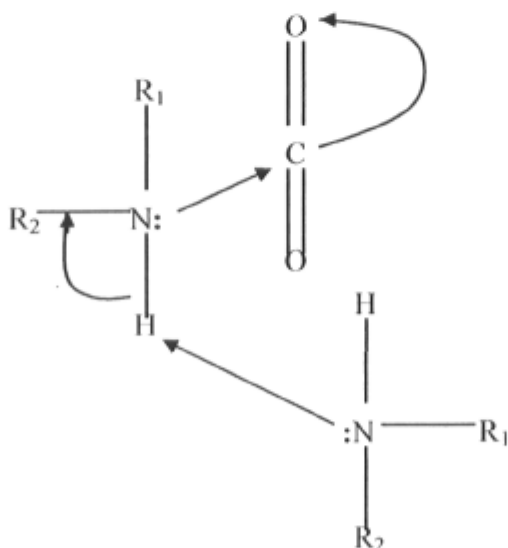
Figure I.2. Schematic drawing of the single step, termolecular reaction mechanism for the formation of carbamates according to Crooks and Donnellan [15]. The amines represented here are secondary amines. In the case of primary amines, R_2 corresponds to H.

It can be seen from the reactions (I.1)-(I.8) and Figure I.2 that the global reaction between CO_2 and primary and secondary amines is as follows:

1. For primary amines:

$$2RNH_2 + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ \tag{I.9}$$

2. For secondary amines:

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{I.10}$$
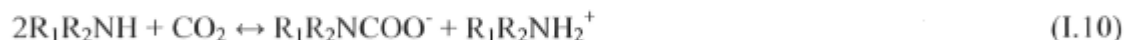
Then, two molecules of primary or secondary amines are needed to absorb one molecule of CO_2. At higher partial pressures of CO_2, a low carbamates hydrolysis occurs. The carbamates hydrolysis forms bicarbonate (HCO_3^-) and generate free amines that can react with additional CO_2. However, the absorption of CO_2 with primary and secondary amines is still limited to 1 mole of CO_2/1 mole of amine by the stoichiometry of the reactions. The carbamates hydrolysis is represented by the following reaction:

1. For primary amines:

$$RNHCOO^- + H_2O \leftrightarrow HCO_3^- + RNH_2 \tag{I.11}$$

2. For secondary amines:

$$R_1R_2NCOO^- + H_2O \leftrightarrow HCO_3^- + R_1R_2NH \tag{I.12}$$

At elevated pH (> 10), the bicarbonate ion (HCO_3^-) forms the carbonate ion (CO_3^{2-}) by the following reaction:

1. For primary amines:

$$HCO_3^- + RNH_2 \leftrightarrow RNH_3^+ + CO_3^{2-} \tag{I.13}$$

2. For secondary amines:

$$HCO_3^- + R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + CO_3^{2-} \tag{I.14}$$

Then, one supplementary molecule of primary or secondary amines is needed to form the carbonate ion (CO_3^{2-}).

Tertiary amines lack of N-H bond required to form carbamates ion and therefore do not react directly with CO_2. However, in aqueous solutions, tertiary amines promote the hydrolysis of CO_2 to form the bicarbonate and the protonated amine by the following reaction:

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^- \qquad (I.13)$$

Then, one molecule of tertiary amine is needed to absorb one molecule of CO_2. Thus, the CO_2 loading capacities of aqueous solutions of tertiary amines are higher than the CO_2 loading capacities of aqueous solutions of primary and secondary amines. The aqueous solutions of tertiary amines are also more easily regenerated by heating than the aqueous solutions of primary and secondary amines which leads to lower energy requirement for regeneration [25]. This is due to the lower heat of reaction of tertiary amines with CO_2. However, the kinetic of the reaction of CO_2 with tertiary amines is very low compared to primary and secondary amines and limits their industrial applications.

I.2.2 Sterically hindered amines

Recently, the use of aqueous solutions of sterically hindered amines has become of great interest as potential post-combustion CO_2 absorbent. A sterically hindered amine is defined structurally as a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or a tertiary carbon atom [26]. Due to the bulkiness of carbon groups attached to the amino group, the sterically hindered amines form unstable carbamates. Then, carbamates hydrolysis occurs, forms bicarbonate and generates free amines that can react with additional carbon dioxide and allows absorption up to 1 mol of CO_2/mol of amine [7,26,27].

The aqueous solutions of sterically hindered amines have also the advantage to have relatively high absorption rates at high CO_2 loadings [26,28,29]. Moreover, contrary to the aqueous solutions of conventional primary and secondary amines, the aqueous solutions of

sterically hindered amines can be easily regenerated by heating and have degradation resistance advantages. This is due to the lower enthalpy of reactions associated to bicarbonate and carbonate ions in the aqueous solutions of sterically hindered amines than the enthalpy of reaction associated with the formation of carbamate ions in the aqueous solutions of primary and secondary amines [7,26,28-30]. Thus, the aqueous solutions of sterically hindered amines have a high cyclic capacity and can be used for a higher number of cycles in the CO_2 scrubbers than the aqueous solutions of primary and secondary amines. Also, the concentrated aqueous solutions of MEA are highly corrosive and generate supplementary cost for the equipment. The aqueous solutions of MEA also show higher vaporization losses due to a higher vapor pressure [31-34].
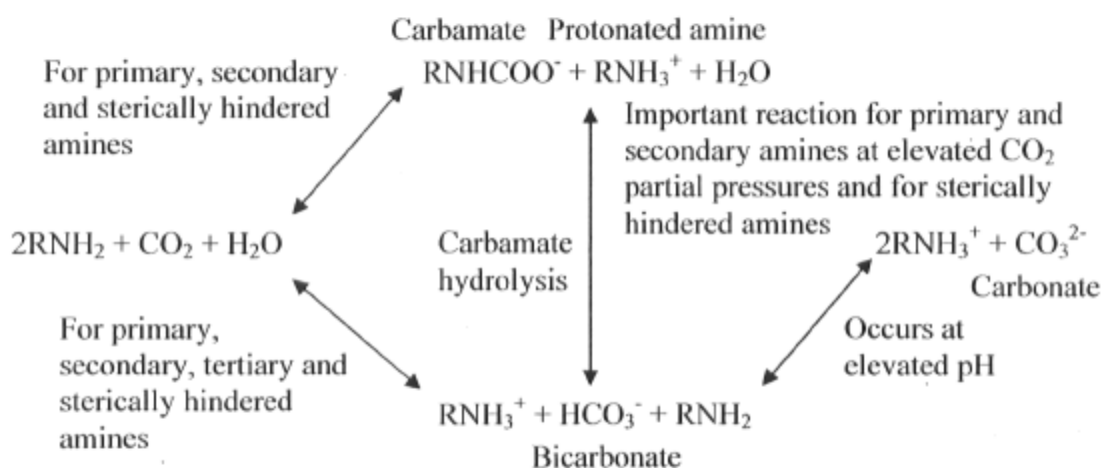
Figure I.3. Chemical reactional mechanisms in a system CO_2-amines-H_2O. In this figure, a primary amine (RNH_2) was taken as example.

The different chemical reactional mechanisms in a system CO_2-amines-H_2O are summarized in Figure I.3. It can be noted from Figure I.3 that the final products are mainly HCO_3^-, RNH_3^+, RNH_2 for aqueous solutions of primary sterically hindered amines ($R_1R_2NH_2^+$, R_1R_2NH for aqueous solutions of secondary sterically hindered amines) with low amounts of $RNHCOO^-$ ($R_1R_2NCOO^-$ in aqueous solutions of secondary sterically hindered amines), CO_3^{2-}, H^+ and OH^- while the final products are mainly HCO_3^-, RNH_3^+, RNH_2 and $RNHCOO^-$ in aqueous solutions of primary amines ($R_1R_2NH_2^+$, R_1R_2NH and $R_1R_2NCOO^-$ in aqueous solutions of secondary amines) with low amounts of CO_3^{2-}, H^+ and

OH^-. The final products for aqueous solutions of tertiary amines are mainly $R_1R_2R_3NH^+$, HCO_3^- and $R_1R_2R_3N$ with low amounts of CO_3^{2-}, H^+ and OH^-.

I.3 Solubility of carbon dioxide in aqueous alkanolamine solutions

I.3.1 Conventional primary, secondary and tertiary amines and their blends

In industrial CO_2 absorption processes, MEA, DEA and MDEA are the most commonly used absorbents. So, the solubility of CO_2 in aqueous solutions of these alkanolamines has been the subject of extensive experimental studies (MEA [35-43]; DEA [30,35,36,38,44-49]; MDEA [37-39,40,50,51-58]). The experimental data presented in these studies are generally for temperatures ranging from (293.15 to 353.15) K, for amine concentrations ranging from (1.5 to 4) M (approximately between amine mass fractions of (10 and 45) %) and for a wide range of CO_2 partial pressures from below 1 kPa to 300 kPa and for some studies up to 1000 kPa. From these studies, it was found that for a same concentration of amine in the solutions and for a same temperature, the solubility of CO_2 is generally higher in aqueous solutions of MEA than in aqueous solutions of DEA and MDEA. However, at medium and elevated CO_2 partial pressures, the solubility of CO_2 is higher in aqueous solutions of MDEA since the advantage of this amine is its high equilibrium loading capacity (up to 1 mol of CO_2 per mole of amine) because this amine does not form carbamate. The CO_2 partial pressure for which the solubility of CO_2 begins to be higher in aqueous solutions of MDEA than in aqueous solutions of MEA depends strongly on the experimental conditions. For an aqueous solution with an amine mass fraction of 30 % at 313.15 K, this CO_2 partial pressure is around 15 kPa and around 220 kPa at 353.15 K [40].

In the past few years, aqueous solutions of mixed alkanolamines, which are blends of primary or secondary amines with a tertiary alkanolamine, have received increasing attention for the removal of CO_2 from different gas streams. Blends of primary and tertiary amines (such as mixtures of MEA and MDEA) or secondary and tertiary amines (such as mixtures of DEA and MDEA) combine the higher equilibrium capacity of the tertiary amine with the higher reaction rate of the primary or secondary amine [30,59-61].

Moreover, since MDEA does not form carbamates, the regeneration costs of aqueous solutions of blends of MEA + MDEA or DEA + MDEA may be lower than aqueous solutions of MEA and DEA. Thus, the use of blended amine solvents, requiring lower circulation rates and lower regeneration energy, can bring about considerable improvement and great savings in individual gas-treating processes [30,60,61].

The solubility of CO_2 in aqueous blends of MEA + MDEA and DEA + MDEA has been also studied extensively [37,40,45,56,59,62,63]. The experimental data presented in these studies are usually for a total amine mass fraction of 30 % (around 3.5 M) for temperatures ranging from (293.15 to 353.15) K and for CO_2 partial pressures ranging from below 1 kPa to 300 kPa and for some studies up to 1000 kPa. From these studies, it was found that an increase in concentration of MDEA in the blends decreases the solubility of CO_2 in the solutions at low partial pressures of CO_2, but increases the solubility at medium and elevated partial pressures of CO_2. The CO_2 partial pressure for which the CO_2 solubility begins to be higher in aqueous mixtures of MEA and MDEA or DEA and MDEA than in aqueous solutions of MEA or DEA depends strongly on the experimental conditions. For example, the CO_2 solubility curves in aqueous 4 M MDEA, 2 M MDEA + 2 M MEA and 4 M MEA cross each other for a CO_2 partial pressure around 80 kPa at 313.15 K, but at 353.15 K this pressure is around 1000 kPa [37]. For aqueous 4 M MDEA, 2 M MDEA + 2 M DEA and 4 M DEA, the CO_2 solubility curves also cross each other for a CO_2 partial pressure around 80 kPa at 313.15 K and also 1000 kPa at 353.15 K [37].

Density and viscosity are important physical properties of aqueous alkanolamine solutions for the analysis of experimental absorption rate, for the rational design of gas absorption units and for mass transfer rate modeling of absorption and regeneration because these properties influence the values of the liquid side mass transfer coefficient, k_L. Then, the density and viscosity of aqueous solutions of MEA, DEA and MDEA and their blends have also been extensively studied [25,62,64-81]. The experimental data presented in these studies are generally for temperatures ranging from (293.15 to 353.15) K and for amine concentrations ranging from (1.5 to 4) M (approximately between amine mass fractions of (10 and 45) %). The density and viscosity of aqueous solutions of alkanolamines increase with decreasing temperature and increasing alkanolamines concentrations.

I.3.2 Other primary, secondary and tertiary amines

Recently, other alkanolamines such as di-glycol-amine (DGA)-[$NH_2(CH_2)_2O(CH_2)_2OH$], 2-(butylamino)ethanol-amine (BEA)-[$CH_3(CH_2)_3NH-(CH_2)_2OH$], 2-(methylamino)ethanol-amine (MMEA)-[$CH_3NH(CH_2)_2OH$], 2-(ethylamino)ethanol-amine (EMEA)-[$CH_3CH_2NH(CH_2)_2OH$], di-*iso*-propanol-amine DIPA-[$(CH_3CHOHCH_2)_2NH$], morpholine (MOR)-[$-O(CH_2)_2NH(CH_2)_2-$], 2-((2-aminoethyl)amino)ethanol-amine (AEEA)-[$H_2N(CH_2)_2NH(CH_2)_2OH$], and triisopropanolamine (TIPA)-[$(CH_3CHOHCH_2)_3N$] were studied by different research groups being some potentially new solvents for post-combustion CO_2 absorbents [1,35,82-84]. DGA is a primary amine and BEA, MMEA, EMEA, DIPA, and MOR are secondary amines. AEEA is a diamine and contains a primary and a secondary amino groups. TIPA is a tertiary amine.

Ma'mun et al. [1] studied the solubility of CO_2 in aqueous solutions of BEA, MMEA, EMEA, AEEA and piperazine (PZ)-[$-NH(CH_2)_2NH(CH_2)_2-$], a cyclic diamine with two secondary amino groups. The solubility of CO_2 in these aqueous solutions was compared with the solubility of CO_2 in aqueous solutions of MEA and MDEA. The absorption of CO_2 was studied at 313.15 K using both single and mixed amine-based absorbents. The experimental results from this study show that most absorbents tested have a poorer performance than MEA, but that aqueous AEEA might be a possible contender. It offers a high absorption rate combined with high absorption capacity compared to the other absorbents used in this study and it maintains its absorption power at higher loadings [1]. Furthermore, the vapor pressure of AEEA is much lower compared to that of MEA. In addition to the absorption measurements, the vapor-liquid equilibrium of CO_2 in the aqueous 2.9 M AEEA was studied at (313.15 and 393.15) K. It was found that the equilibrium partial pressures of CO_2 in the aqueous 2.9 M AEEA at the temperature of removal (313.15 K) and that of regeneration (393.15 K) are lower than for aqueous 5.0 M MEA, but the maximum net cyclic capacity is somewhat higher. Another study of Ma'mun et al. [82] focuses on the experimental determination of the solubility of CO_2 in an aqueous solution of 30 mass % AEEA for partial pressures of CO_2 ranging from 0.01 to 220 kPa at temperatures ranging from (313.15 to 393.15) K.

Van Loo et al. [35] studied the removal of carbon dioxide in activated aqueous solutions of MDEA. The activators/accelerators used were MEA, DEA, MMEA, DGA, DIPA and 2-amino-2-methyl-1-propanol (AMP)-[NH_2C-$(CH_3)_2CH_2OH$]. AMP is a primary sterically hindered amine. The study has been executed with respect to the performance of CO_2 removal from natural gas. The absorption process has been simulated in a tray column. From these simulations, the optimal number of trays in combination with the amount of activator-addition can be established.

Al-Juaied and Rochelle [83] studied the solubility of CO_2 in aqueous solutions of DGA, MOR and blends of DGA and MOR. In this study, the solubility of CO_2 was measured in aqueous solutions of 3.5 M (23.5 mass %) MOR, 17.7 M (65 mass %) DGA, and 3.6 M MOR + 14.7 M DGA (11 mass % MOR + 53 mass % DGA) at 298.15, 313.15 and 333.15 K and for CO_2 partial pressures ranging from 0.005 to 53.7 kPa. It was found that at a given CO_2 loading (mol CO_2/mol amine), the CO_2 vapor pressure over 3.5 M MOR is 10 to 1000 times greater than 17.7 M DGA and is also greater than 3.6 M MOR + 14.7 M DGA. In 3.6 M MOR + 14.7 M DGA, the CO_2 vapor pressure is 5 to 7 times greater than in 17.7 M DGA at high CO_2 loading, but the same below 0.2 loading. The working capacity of the blend is 17 % less than 17.7 M DGA.

Chauhan et al. [84] measured the solubility of CO_2 in aqueous solutions of TIPA at (313.15, 323.15 and 333.15) K and over CO_2 partial pressures ranging from (1 to 3000) kPa. The treated TIPA mass fractions of aqueous solutions were (10 and 30) %. The solubility of CO_2 in aqueous 30 mass % TIPA at 333.15 K were compared with those in aqueous solutions of MEA and MDEA. It was found that the loading capacity of aqueous TIPA solutions is higher than that of aqueous MEA and MDEA solutions at higher partial pressures of CO_2, while is lower at low and medium pressures. For 30 mass % aqueous alkanolamine solutions at 333.15 K, the partial pressure of CO_2 for which the solubility of CO_2 becomes higher in aqueous solutions of TIPA than that in aqueous solutions of MEA and MDEA is around 100 kPa. This pressure varies with the equilibrium temperature and concentration of amines in the solutions.

I.3.3 Aqueous alkanolamines solutions promoted with piperazine

Absorption of CO_2 in aqueous solutions of piperazine (PZ)-$[-NH(CH_2)_2NH(CH_2)_2-]$ [1,85,86] and in blends of PZ + MDEA [51,54,85,87] was studied by different research groups. The density and viscosity of aqueous blends of PZ + MDEA were also measured in a few studies [25,79,88]. Piperazine is commonly used as an activator for aqueous solutions of MDEA [89]. Being a cyclic symmetric diamine in a six-membered saturated ring and having two secondary amino groups, piperazine can theoretically absorb 2 mol of CO_2 for every mol of amine, and it favours rapid formation of the carbamates [90-92]. The rate constant of PZ has been found to be one order of magnitude higher than that of conventional alkanolamines such as MEA [93]. PZ-activated aqueous MDEA solutions have also the advantage to combine the relatively high rate of reaction of the former with CO_2 with the lower heat of reaction of the later with CO_2.

Jenab et al. [87] studied the solubility of CO_2 in aqueous mixtures of MDEA + PZ at (313.15, 328.15 and 343.15) K. The compositions of the aqueous mixtures studied were (3 M MDEA + 0.36 M PZ), (2.5 M MDEA + 0.86 M PZ) and (2 M MDEA + 1.36 M PZ). Their results show that the absorption of CO_2 increases with an increasing of PZ concentration in the aqueous mixtures. The increase of CO_2 solubility with increasing PZ concentration in the mixtures seems to occur progressively with CO_2 partial pressure.

Liu et al. [54] also studied the solubility of CO_2 in aqueous mixtures of MDEA + PZ. The compositions of the aqueous mixtures studied and the temperatures were (1.53 M MDEA + 0.17 M PZ) and (1.35 M MDEA + 0.35 M PZ) at (323.15 and 343.15) K; (3.15 M MDEA + 0.35 M PZ) and (2.8 M MDEA + 0.7 M) at (303.15, 323.15, 343.15 and 363.15) K; (4.77 M MDEA + 0.53 M PZ) and (3.75 M MDEA + 1.55 M PZ) at (323.15 and 343.15) K. Their results also show that the solubility of CO_2 increases with an increase in PZ concentration of the aqueous mixtures. This effect seems to increase progressively with CO_2 partial pressure as in the case of Jenab et al. [87]. Another study from Xu et al. [51] also pointed out that the solubility of CO_2 increases with an increasing of PZ concentration of aqueous mixtures of MDEA + PZ.

Aroua and Salleh [86] measured the solubility of CO_2 in aqueous solutions of PZ for PZ concentrations of (0.1, 0.2, 0.4, 0.6 and 1.0 and 2.0) M at (293.15, 303.15, 313.15 and 323.15) K with CO_2 partial pressures ranging from (0.4 to 95) kPa. They also compared the solubility of CO_2 in a 2.0 M PZ aqueous solution at 303.15 K with the solubility of CO_2 in aqueous solutions of MDEA and DEA. Their results show that the solubility of CO_2 is higher in aqueous solutions of PZ than in aqueous solutions of MDEA and DEA for CO_2 partial pressures below 12 kPa, but is lower for CO_2 partial pressures up to 12 kPa. The study of Ma'mun et al. [1] presented in the above section showed that aqueous solutions of PZ have a poorer performance than the aqueous solutions of MEA.

From these experimental results, it can be concluded that the solubility of CO_2 in aqueous solutions of PZ doesn't seem to be higher than the solubility of CO_2 in aqueous solutions of MDEA and DEA for all experimental conditions and seems to be lower than the solubility of CO_2 in aqueous solutions of MEA. However, PZ seems to be an effective promoter for aqueous solutions of MDEA.

I.3.4 Sterically hindered amines

I.3.4.1 A primary sterically hindered amine: 2-amino-2-methyl-1-propanol (AMP)

In industrial CO_2 absorption processes, 2-amino-2-methyl-1-propanol (AMP)-[NH_2C-$(CH_3)_2CH_2OH$] is the most common sterically hindered amine used as absorbent. AMP is a primary sterically hindered amine. The solubility of CO_2 in aqueous solutions of AMP has been the subject of extensive experimental studies [7,30,35,36,44,46,48,53,55,94-97]. The density and viscosity of aqueous solutions of AMP were also measured [24,64,71,72,74,89,98-100]. The experimental data presented in these studies are generally for temperatures ranging from (293.15 to 353) K, for AMP concentrations ranging from (2 to 3.4) M (approximately between (18 to 30) mass %) and for CO_2 partial pressures ranging from (0.1 to 200) kPa and for some studies up to 1000 kPa.

It was found that the solubility of CO_2 is lower in aqueous solutions of AMP than in aqueous solutions of MEA for low CO_2 partial pressures, but is higher for medium and elevated CO_2 partial pressures. The CO_2 partial pressure for which the solubility of CO_2 is

higher in aqueous solutions of AMP than in aqueous solutions of MEA depends strongly on the temperature and amine concentration of the solutions. For an aqueous solution with an amine mass fraction of 30 %, the solubility of CO_2 becomes higher in aqueous solutions of AMP than in aqueous solutions of MEA for a CO_2 partial pressure around 3 kPa at 313.15 K and around 59 kPa at 353.15 K corresponding to a CO_2 loading (α) in the solutions of 0.5 mol of CO_2/mol amine [36]. This is primarily due to the fact that AMP forms a very unstable carbamate upon reaction with CO_2 and requires one amine molecule for each CO_2 molecule reacted. However, the reaction between MEA and CO_2 forms very stable carbamates, which could not be converted to bicarbonate and remain in the solution, resulting in the conversion of two amine molecules for each reacted CO_2 molecule. Hence, for an aqueous solution of MEA, it is reasonable to assume that the amine would completely convert to products at CO_2 loading greater than 0.5 mol of CO_2/mol of amine, and the sudden change of equilibrium partial pressure occurs because of physical absorption rather than chemical absorption. However, for CO_2 loading lower than 0.5 mol of CO_2/mol of amine, the solubility of CO_2 in aqueous solutions of MEA is higher since MEA can react better than AMP with CO_2 because the reactivity of MEA with CO_2 is greater than that of AMP [36].

From the previous mentioned studies, it was established that the solubility of CO_2 in aqueous solutions of AMP is higher than that in aqueous solutions of DEA for medium and elevated CO_2 partial pressures. For low CO_2 partial pressures, approximately below (0.7 and 7) kPa at (313.15 and 333.15) K, respectively, the solubility of CO_2 in aqueous solutions of DEA and AMP are close and are sensibly the same [36]. This is due to the fact that DEA, being a secondary alkanolamine, is not as reactive with CO_2 as MEA, and it represents higher equilibrium partial pressures of CO_2 at low CO_2 loading. DEA nearly has the same tendency to absorb CO_2 like AMP at low CO_2 loading, but the solubility of CO_2 in aqueous solutions highly depends on temperature. Then, at 353.15 K, the solubility of CO_2 in aqueous solutions of DEA is higher than that in aqueous solutions of AMP for CO_2 partial pressures below 70 kPa, corresponding to a CO_2 loading of 0.5 mol of CO_2/mol of amine [36,44].

Finally, from the previous studies, it was also found that the solubility of CO_2 in aqueous solutions of AMP is better than that in the aqueous solutions of MDEA for the whole range of temperatures and CO_2 partial pressures studied in the literature. This is due to the fact that AMP forms unstable carbamates and the most part of these carbamates hydrolyse to form bicarbonate and that MDEA does not form carbamates. So, the loading capacity of AMP and MDEA are sensibly the same, around 1mol of CO_2/mol of amine, and the reactivity of AMP with CO_2 is higher than that of MDEA. However, for CO_2 partial pressures up to 100 kPa at 303.15 K and for an amine concentration in the solution of 2 M, the solubility of CO_2 in these aqueous solutions are close and sensibly the same [53].

I.3.4.2 Blends of AMP with conventional primary, secondary and tertiary amines

The use of blends of primary or secondary amines with sterically hindered amines in gas-treating processes is of great interest today. As in the case of blends of primary and tertiary amines (MEA+MDEA) or secondary and tertiary amines (DEA+MDEA), the blends of primary or secondary amines with sterically hindered amines combine the higher equilibrium capacity of the sterically hindered amines with the higher reaction rate of the primary or secondary amines with CO_2. However, compared to MDEA, AMP has the same high equilibrium capacity for CO_2, but has a reaction higher rate constant for CO_2 [28]. Since sterically hindered amine like AMP does not form stable carbamate, bicarbonate and carbonate ions may be present in the solution in larger amounts than the carbamates ions. Hence, the regeneration energy costs when aqueous solutions of AMP are used to absorb CO_2 may be lower as in the case of using aqueous MDEA solutions. Hence, aqueous blends of AMP and MEA may be an attractive new alternative solvent to aqueous blends of MDEA and MEA for the gas-treating processes.

The solubility of CO_2 in aqueous blends of AMP + MEA [36,95], AMP + DEA [30,36,44,46,59], AMP + MDEA [53] and AMP + MDEA + DEA [45,101] were studied. The density and viscosity of aqueous blends of AMP with MEA, DEA or MDEA were also measured [24,64,65,67,68,71-74,99,102]. The experimental data presented in these studies are generally for a total amine mass fraction in the solutions of 30 %, for temperatures ranging from (293.15 to 353) K, and for CO_2 partial pressures ranging from (0.1 to 200) kPa and for some studies up to 1000 kPa. It was found that an increase in AMP

concentration in aqueous blends of AMP + MEA decreases the solubility of CO_2 in aqueous solutions at low partial pressures of CO_2, corresponding to a CO_2 loading below 0.5 mol of CO_2/mol of amine, but increases the solubility of CO_2 in aqueous solutions at medium and elevated partial pressures of CO_2, corresponding to a CO_2 loading up to 0.5 mol of CO_2/mol of amine.

It was found that increasing AMP concentration in aqueous blends of AMP + DEA increases the solubility of CO_2 at medium and elevated CO_2 partial pressures while for low CO_2 partial pressures, approximately below (0.7 and 7) kPa at (313.15 and 333.15) K, respectively, the solubility does not seem to be significantly influenced by the concentration of the blends [36]. However, at 353.15 K, an increase in AMP concentration in the blends increases the solubility of CO_2 at elevated CO_2 partial pressures, but decreases the solubility of CO_2 for low and medium CO_2 partial pressures (below 70 kPa corresponding to a CO_2 loading of 0.5 mol of CO_2/mol of amine) [36,44]. So, the blends of AMP + DEA doesn't seem to be advantageous for the solubility of CO_2 in aqueous solutions since the solubility of CO_2 is higher in aqueous solutions of AMP than that in aqueous solutions of DEA, except if the temperature is 353.15 K. As mentioned previously, this is due tot the fact that DEA, being a secondary alkanolamine, is not as reactive to CO_2 as MEA and has the same tendency to absorb CO_2 like AMP at low CO_2 loading.

As mentioned above in the section I.3.4.1, the solubility of CO_2 in aqueous solutions of AMP is higher than that in aqueous solutions of MDEA. So, it was also found that aqueous blends of AMP + MDEA are not advantageous for CO_2 capture [53].

I.3.4.3 Other primary sterically hindered amines

Other primary sterically hindered amines like 2-amino-2-methyl-1,3-propanediol (AMPD)-[$NH_2C(CH_2OH)_2CH_3$], 2-amino-2-ethyl-1,3-propanediol (AEPD)-[$NH_2C-(CH_2OH)_2CH_2CH_3$] and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)-[$NH_2C-(CH_2OH)_3$] were also studied as potential CO_2 absorbents [41-43,103]. The density and viscosity of these aqueous solutions were also measured [42,104,105]. However, the results about the solubility of CO_2 in these aqueous solutions are still scarce and are only available for limited range of experimental conditions. The solubility of CO_2 in aqueous solutions of

AMPD was then measured for AMPD mass fractions of (10 and 30) % at (303.15, 313.15 and 333.15) K and for CO_2 partial pressures ranging from (0.5 to 3065) kPa [103]. The solubility of CO_2 in aqueous solutions of AEPD was measured for AEPD mass fractions of (10 and 30) % at (313.15, 323.15 and 333.25) K and for CO_2 partial pressures ranging from (1 to 3000) kPa [41]. The solubility of CO_2 in aqueous AHPD solutions was measured for AHPD mass fractions of (10 and 20) % at (313.15, 323.15 and 333.15) K and for CO_2 partial pressures ranging from (20 to 2000) kPa [42]. It was also measured for AHPD mass fraction of 10 % at 298.15 K and for CO_2 partial pressures ranging from (0.09 to 2427) kPa [43].

The study of Park et al. [41] compares the solubility of CO_2 in aqueous 30 mass % alkanolamine solutions at 333.15 K. The different alkanolamine are AEPD, AMPD, AMP, MDEA and MEA. It was found that the solubility curve of CO_2 in an aqueous solution of MEA crosses the solubility curve of CO_2 in an aqueous solution of :

- AMP around a CO_2 partial pressure of 20 kPa corresponding to a CO_2 loading (α) around 0.53 mol of CO_2/mol of amine,

- MDEA around a CO_2 partial pressure of 70 kPa corresponding to a $\alpha \approx 0.57$,

- AEPD around a CO_2 partial pressure of 90 kPa corresponding to a $\alpha \approx 0.6$,

- AMPD around a CO_2 partial pressure of 110 kPa corresponding to a $\alpha \approx 0.61$.

These results mean that the solubility of CO_2 in aqueous solutions of MEA is higher for low CO_2 partial pressures but lower than that of MDEA and sterically hindered amines for high CO_2 partial pressures. This study also shows that the CO_2 loading capacity of an aqueous solution of MDEA seems to be better than that of aqueous solutions of AEPD and AMPD for the whole range of CO_2 partial pressures measured in this study (between 1 to 3000 kPa). The solubility of CO_2 in aqueous solutions of AEPD and AMPD are close for the whole range of CO_2 partial pressures studied. However, the solubility of CO_2 in an aqueous solution of AEPD is slightly lower for CO_2 partial pressures below 80 kPa and slightly higher for CO_2 partial pressures up to 80 kPa. The solubility of CO_2 in an aqueous solution of AMP can not be compared to those in aqueous solutions of AEPD, AMPD and

MDEA for CO_2 partial pressures up to 300 kPa since the solubility of CO_2 in this solution was not measured. However, the solubility of CO_2 in this solution is higher that those in aqueous solutions of AEPD, AMPD, MDEA for CO_2 partial pressures between 2 to 300 kPa and lower than that of an aqueous solution of MDEA for CO_2 partial pressures below 2 kPa.

The study of Park et al. [42] compared the solubility of CO_2 in an aqueous solution of AHPD at 313.15 K for CO_2 partial pressures from (20 to 2000) kPa to those in aqueous solutions of AEPD, AMPD and MEA. At elevated CO_2 partial pressures, it was found that the solubility of CO_2 in aqueous alkanolamine solutions decreases from AHPD to AEPD, AEPD to AMPD and AMPD to MEA. However, as CO_2 partial pressures decrease, the solubility of CO_2 in an aqueous AHPD solution decreases rapidly and becomes lower than that in an aqueous solution of AEPD around 120 kPa, an aqueous solution of AMPD around 100 kPa and eventually an aqueous solution of MEA below 50 kPa. From these results and those presented in the previous study [41], it seems that an increase in the steric hindrance of the amines (AMPD < AEPD <AHPD) increases the loading capacity of these amines at elevated CO_2 partial pressures.

I.3.5 Discussion and conclusion

From the CO_2 data presented in the above mentioned studies, the following observations can be made. The solubility of CO_2 in aqueous solutions of alkanolamines expressed in term of α (moles of CO_2 totally (chemically and physically) absorbed/mole of alkanolamines) decreases with:

- decreasing partial pressure of CO_2 (at constant temperature and amine concentration)

- increasing temperature (at constant partial pressure of CO_2 and amine concentration)

- increasing amine concentration in the aqueous solutions (at constant temperature and partial pressure of CO_2). However, it was observed that if the solubility of CO_2 in aqueous solutions of alkanolamines is expressed in terms of molarity (M

(mol/L)), the solubility of CO_2 increases with increasing amine concentration in the aqueous solutions.

The solubilities of CO_2 in aqueous solutions of conventional tertiary (MDEA) and sterically hindered amines are higher than those in aqueous solutions of conventional primary (MEA) and secondary (DEA) amines at elevated CO_2 partial pressures, but poorer for lower CO_2 partial pressures. The solubility of CO_2 is higher in aqueous solutions of MEA than that in aqueous solutions of DEA. Piperazine (PZ) is an effective promoter for aqueous solutions of MDEA since an increase in PZ concentration in aqueous blends of PZ and MDEA increases the solubility of CO_2.

In the past few years, aqueous blends of primary (MEA) or secondary (DEA) amine with a tertiary alkanolamine (MDEA), have received increasing attention for the removal of CO_2 from different gas streams. These blends combine the higher equilibrium capacity of the tertiary amine with the higher reaction rate of the primary or secondary amine. Moreover, since MDEA does not form carbamates, the regeneration costs of aqueous solutions of blends of MEA + MDEA or DEA + MDEA may be lower than those for aqueous solutions of MEA and DEA. Thus, the use of blended amine solvents, requiring lower circulation rates and lower regeneration energy, can bring about considerable improvement and great savings in individual gas-treating processes.

Recently, blends of sterically hindered amines with conventional primary or secondary amines like AMP + MEA and AMP + DEA have also received increasing interest as CO_2 absorbents. Compared to MDEA, AMP has the same high equilibrium capacity for CO_2, but has a higher rate constant for reaction with CO_2. The regeneration energy costs when aqueous solutions of AMP are used to absorb CO_2 may be lower as in the case of using aqueous MDEA solutions since AMP forms unstable carbamates. Then, aqueous blends of AMP with MEA may be a new alternative solvent to aqueous blends of MDEA and MEA for gas-treating processes.

Other primary sterically hindered amines like AMPD, AEPD and AHPD were also studied as CO_2 absorbents. However, the studies about the solubility of CO_2 in these aqueous solutions are still scarce, and the solubility of CO_2 in these aqueous solutions is available

for limited experimental conditions. From these results, it seems that an increase in the steric hindrance of the amine (AMPD < AEPD < AHPD) increases the loading capacity at elevated CO_2 partial pressures while the solubility of CO_2 decreases for lower CO_2 partial pressures.

I.4 Gas-Liquid Equilibrium Models for Systems containing CO_2 + Alkanolamines + H_2O

Some models have been developed in the literature to represent and to predict the vapor-liquid equilibrium of the solubility of CO_2 in aqueous alkanolamines solutions. These models generally allow the calculation of the concentration of species present in the aqueous alkanolamines solutions at the equilibrium and the determination of the amine deprotonation constant and the carbamate stability constant. These two constants were found to be functions of temperature, CO_2 loading and amine concentration and are presented in the next chapter.

The models typically used to represent and to predict the vapor-liquid equilibrium for systems containing CO_2 + alkanolamines + H_2O are the models of Kent-Eisenberg [106] and Deshmukh-Mather [107]. The model developed by Kent and Eisenberg is a simple thermodynamic model using apparent equilibrium constants. It assumes that all activity coefficients and fugacity coefficients to be unity except for the species intervening in the amine-related apparent equilibrium. The model of Desmukh-Mather is more complicated than the model of Kent-Eisenberg. This model is based on the extended Debye-Hückel theory of electrolyte solutions. It involves the determination of the activity coefficients (γ_i) of each species present in the aqueous alkanolamine solutions at the equilibrium, which are calculated by the extended Debye-Hückel equation, and also the determination of the fugacity coefficients (φ_i) for all volatile components which are usually calculated using the Peng-Robinson equation of state for the gaseous phase.

Other studies use the modified Clegg-Pitzer equations [108,109] to derive the activity coefficients of different species present in the equilibrated liquid phase. More complex models such as the electrolyte-NRTL, the electrolyte-UNIFAC/UNIQUAC or the electrolyte-linear combination of the Vidal and Michelsen mixing rules (e-LCVM) models

are sometimes used. The electrolyte-NRTL model in acid gases (H_2S and CO_2) + alkanolamines + H_2O systems has been described by Austgen [110], Posey [111] and Bishnoi and Rochelle [112]. The electrolyte-LCVM model was presented by Vrachnos et al. [113,114]. The advantage of the electrolyte-NRTL, the electrolyte-UNIFAC/UNIQUAC and the electrolyte-LCVM models is that, because it is basically an Equation of State (EoS) approach, it describes all phases at equilibrium consistently with the same equation. It can also be applied to phase equilibrium calculations to provide estimations of some mixture properties, such as the volumetric behaviour of acid gas-alkanolamines-H_2O mixtures, which is very important information for the design of absorption columns. However, these models are also more computationally expensive without offering a better fit of vapor-liquid equilibrium data or species concentrations [82].

In the present work, the Kent-Eisenberg model was chosen as the base model because it had given a good performance for the correlation and prediction of CO_2 solubility in alkanolamine solutions in previous studies [7,36,63,95] and also for other reasons related to the experimental conditions explained in the next chapter. More detailed information about the thermodynamic model developed here including all equilibrium reactions, equations and amine deprotonation constant and carbamate stability constant are also presented in the next chapter.

I.5 Objectives

The objective of this work was to determine the solubility of CO_2 into aqueous solutions of 2-amino-2-hydromethyl-1,3-propanediol (AHPD), as a function of different temperatures, CO_2 partial pressures and AHPD concentrations of solutions. The solubility of CO_2 was measured for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at (283.15, 298.15 and 313.15) K and for carbon dioxide partial pressures ranging from approximately (2 to 75) kPa. To our knowledge, no similar solubility data were reported in the open literature for these experimental conditions. These experimental conditions are very important since they were chosen in direct connection to specific industrial conditions for an enzymatic CO_2 capture process involving the use of a zinc-bearing cytosolic metalloenzyme (CO_2 Solution Inc.), namely type II human carbonic anhydrase (HCA) [115]. Detailed information about

this industrial process and the importance of the AHPD in this process are provided in the next chapter. In addition, HCA (500 mg/L) was added in the aqueous AHPD solutions for an amine mass fraction of 2.5 % at (283.15, 298.15 and 313.15) K and CO_2 partial pressures below 9 kPa to verify the influence of the enzyme on the solubility of CO_2.

The solubility data of CO_2 measured in aqueous AHPD solutions were used to model the gas-liquid equilibrium for this system. The model developed in this study is based on the model presented in the study of Kent and Eisenberg [106]. This model is very interesting for the prediction of the gas-liquid equilibrium for a system CO_2 + AHPD + H_2O in the range of AHPD concentrations, CO_2 partial pressures and temperatures conditions explored in this study.

In order to validate the solubility apparatus and the experimental procedure, the solubilities of CO_2 and N_2O in water at (283.15, 288.15, 298.15 and 313.15) K were measured and compared with those reported in the literature. The solubility of nitrous oxide (N_2O) in aqueous solutions of AHPD was also measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K. These solubility data were used to estimate the physical solubility of CO_2 in aqueous solutions of AHPD by the N_2O analogy. The determination of the physical solubility of CO_2 in aqueous solutions of AHPD is also essential for the development of the gas-liquid equilibrium model.

Knowledge of the physical properties, for example, density and viscosity, of aqueous solutions of alkanolamines is essential for process design of gas treating units. Solution density and viscosity are also important for the mass transfer rate modeling of absorption and regeneration because these properties influence the values of the liquid side mass transfer coefficient, k_L. So, densities and viscosities of aqueous AHPD solutions were also measured over the temperature range from (283.15 to 313.15) K and at the AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % and 2.5 % with an enzyme concentration of 500 mg/L.

I.6 Literature cited

[1] Ma'mun, S.; Svendsen, H.F.; Hoff, K.A.; Juliussen, O., *Energy Convers. Manage.* 2007, 48, 251-258.

[2] Williams, M., "Climate Change: information kit", *the United Nations Environment Programme (UNEP) and the United Nations Framework Conventions on Climate Change (UNFCCC)*, Geneva, 2002.

[3] Rao, A.B.; Rubin, E.S., *Environ. Sci. Technol.* 2002, 36, 4467-4475.

[4] Suda, T.; Iijima, M.; Tanaka, H.; Mitsuoka, S.; Iwaki, T., *Environ. Prog.* 1997, 16, 200-207.

[5] Hook, R.J., *Ind. Eng. Chem. Res.* 1997, 36, 1779-1790.

[6] Blauwhoff, P.M.M.; Versteeg, G.F.; Van Swaaij, W.P.M., *Chem. Eng. Sci.* 1984, 39, 207-225.

[7] Tontiwachwuthikul, P.; Meisen, A.; Lim, C.J., *J. Chem. Eng. Data* 1991, 36, 130-133.

[8] Niswander, R.H.; Edwards, D.J.; DuPart, M.S.; Tse, J.P., *Sep. Sci. Technol.* 1993, 28, 565-578.

[9] Ma'mun, S.; Dindore, V.Y.; Svendsen, H.F., *Ind. Eng. Chem. Res.* 2007, 46, 385-394.

[10] Danckwerts, P.V.; Sharma, M.M., *Chem. Eng.* 1966, CE244-CE280.

[11] Versteeg, G.F.; Van Dijck, L.A.J.; van Swaaij, W.P.M., *Chem. Eng. Commun.* 1996, 144, 113-158.

[12] Astarita, G.D.; Savage, D.W.; Bisio, A., "Gas treating with chemical solvents", *John Wiley and Sons*, New York, 1983.

[13] Isaacs, E.E.; Otto, F.D.; Mather, A.E., *J. Chem. Eng. Data* 1980, 25, 118-120.

[14] Arstad, B.; Blom, R.; Swang, O., *J. Phys. Chem. A* 2007, 111, 1222-1228.

[15] Crooks, J.E.; Donnellan. J.P., *J. Chem. Soc., Perkin Trans. 2* 1989, 4, 331-333.

[16] Al-Juaied, M.; Rochelle, G.T., *Ind. Eng. Chem. Res.* 2006, 45, 2473-2482.

[17] Caplow, M., *J. Am. Chem. Soc.* 1968, 90, 6795-6803.

[18] Danckwerts, P.V., *Chem. Eng. Sci.* 1979, 34, 443-446.

[19] Versteeg, G.F.; van Swaaij, W.P.M., *Chem. Eng. Sci.* 1988, 43, 587-591.

[20] Little, R.J.; Versteeg, G.F.; van Swaaij, W.P.M., *Chem. Eng. Sci.* 1992, 47, 2037-2045.

[21] Versteeg, G.F.; Kuipers, J.A.M.; Van Beckum, F.P.H.; van Swaaij, W.P.M., *Chem. Eng. Sci.* 1990, 45, 183-197.

[22] Versteeg, G.F.; Oyevaar, M.H., *Chem. Eng. Sci.* 1989, 44, 1264-1268.

[23] Glasscock, D.A.; Critchfield, J.E.; Rochelle, G.T., *Chem. Eng. Sci.* 1991, 46, 2829-2845.

[24] Mandal, B.P.; Biswas, A.K.; Bandyopadhyay, S.S., *Chem. Eng. Sci.* 2003, 58, 4137-4144.

[25] Paul, S.; Mandal, B., *J. Chem. Eng. Data* 2006, 51, 1808-1810.

[26] Sartori, G.; Savage, D.W., *Ind. Eng. Chem. Fundam.* 1983, 22, 239-249.

[27] Chakraborty, A.K.; Astarita, G.; Bischoff, K.B., *Chem. Eng. Sci.* 1986, 41, 997-1003.

[28] Saha, A.K.; Bandyopadhyay, S.S.; Biswas, A.K., *Chem. Eng. Sci.* 1995, 50, 3587-3598.

[29] Say, G.R.; Heinzelmann, F.J.; Iyenger, J.N.; Savage, D.W.; Bisio, A.; Sartori, C., *Chem. Eng. Prog.* 1984, 80, 72-77.

[30] Kundu, M.; Bandyopadhyay, S.S., *J. Chem. Eng. Data* 2006, 51, 398-405.

[31] Bucklin, R.W., *Oil Gas J.* 1982, 204-210.

[32] Li, Y.-G.; Mather, A.E., *Ind. Eng. Chem. Res.* 1994, 33, 2006-2015.

[33] Jou, F.-Y.; Mather, A.E.; Otto, F.D., *Can. J. Chem. Eng.* 1995, 73, 140-147.

[34] Liu, Y.; Zhang, L.; Watanasiri, S., *Ind. Eng. Chem. Res.* 1999, 38, 2080-2090.

[35] Van Loo, S.; Van Elk, E.P.; Versteeg, G.F., *Journal of Petroleum Science and Engineering* 2007, 55, 135-145.

[36] Park, S.H.; Lee, K.B.; Hyun, J.C.; Kim, S.H., *Ind. Eng. Chem. Res.* 2002, 41, 1658-1665.

[37] Austgen, D.M.; Rochelle, G.T.; Chen, C.C., *Ind. Eng. Chem. Res.* 1991, 30, 543-555.

[38] Gabrielsen, J.; Michelsen, M.L.; Stenby, E.H.; Kontogeorgis, G.M., *Ind. Eng. Chem. Res.* 2005, 44, 3348-3354.

[39] Ma'mun, S.; Nilsen, R.; Svendsen, H.F., *J. Chem. Eng. Data* 2005, 50, 630-634.

[40] Shen, K.-P.; Li, M.-H., *J. Chem. Eng. Data* 1992, 37, 96-100.

[41] Park, J.-Y.; Yoon, S.J.; Lee, H.; Yoon, J.-H.; Shim, J.-G.; Lee, J.K.; Min, B.-Y.; Eum, H.-M.; Kang, M.C., *Fluid Phase Equilibria* 2002, 202, 359-366.

[42] Park, J.-Y.; Yoon, S. J.; Lee, H.; Yoon, J.-H.; Shim, J.-H.; Lee, J.K.; Min, B.-Y.; Eum, H.-M., *J. Chem. Eng. Data*, 2002, 47, 970-973.

[43] Park, J.-Y.; Yoon, S.J.; Lee, H., *Environ. Sci. Technol.* 2003, 37, 1670-1675.

[44] Seo, D.J.; Hong, W.H., *J. Chem. Eng. Data* 1996, 41, 258-260.

[45] Rebolledo-Libreros, M.E.; Trejo, A., *Fluid Phase Equilib.* 2004, 218, 261-267.

[46] Jane, I.S.; Li, M.H., *J. Chem. Eng. Data* 1997, 42, 98-105.

[47] Barreau, A.; Blanchon le Bouhelec, E.; Habchi Tounsi, K.N.; Mougin, P.; Lecomte, F., *Oil & Gas Science and Technology* 2006, 61, 345-361.

[48] Haji-Sulaiman, M.Z.; Aroua, M.K.; Ilyas Pervez, M., *Gas Sep. Purif.* 1996, 10, 13-18.

[49] Lal, D.; Otto, F.D.; Mather, A.E., *Can. J. Chem. Eng.* 1985, 63, 681-685.

[50] Huttenhuis, P.J.G.; Agrawal, N.J.; Hogendoorn, J.A.; Versteeg, G.F., *Journal of Petroleum Science and Engineering* 2007, 55, 122-134.

[51] Xu, G.-W.; Zhang, C.-F.; Qin, S.-J.; Gao, W.-H.; Liu, H.-B., *Ind. Eng. Chem. Res.* 1998, 37, 1473-1477.

[52] Ai, N.; Chen, J.; Fei, W., *J. Chem. Eng. Data* 2005, 50, 492-496.

[53] Aroua, M.K.; Haji-Sulaiman, M.Z.; Ramasamy, K., *Separation and Purification Technology* 2002, 29, 153-162.

[54] Liu, H.-B.; Zhang, C.-F.; Xu, G.-W., *Ind. Eng. Chem. Res.* 1999, 38, 4032-4036.

[55] Silkenbäumer, D.; Rumpf, B.; Lichtenthaler, R.N., *Ind. Eng. Chem. Res.* 1998, 37, 3133-3141.

[56] Jou, F.-Y.; Otto, F.D.; Mather, A.E., *Ind. Eng. Chem. Res.* 1994, 33, 2002-2005.

[57] Jou, F.-Y.; Carroll, J.J.; Mather, A.E.; Otto, F.D., *Can. J. Chem. Eng.* 1993, 71, 264-268.

[58] Jou, F.-Y.; Mather, A.E.; Otto, F.D., *Ind. Eng. Chem. Process. Des. Dev.* 1982, 21, 539-544.

[59] Murrieta-Guevara, F.; Rebolledo-Libreros, M.E.; Romero-Martínez, A.; Trejo, A., *Fluid Phase Equilib.* 1998, 150-151, 721-729.

[60] Chakravarty, T.; Phukan, U.K.; Weiland, R.H., *Chem. Eng. Prog.* 1985, 81, 32-36.

[61] Kohl, A.L.; Nielsen, R.B., *Gas Purification*, 5th edition, Gulf Publishing Company: Houston, TX, USA, 1997.

[62] Li, M.-H.; Shen, K.-P., *J. Chem. Eng. Data* 1992, 37, 288-290.

[63] Li, M.-H.; Shen, K.-P., *Fluid Phase Equilib.* 1993, 85, 129-140.

[64] Rebolledo-Libreros, M.E.; Trejo, A., *J. Chem. Eng. Data* 2006, 51, 702-707.

[65] Li, M.-H.; Lie, Y.-C., *J. Chem. Eng. Data* 1994, 39, 444-447.

[66] Hagewiesche, D.P.; Ashour, S.S.; Sandall, O.C., *J. Chem. Eng. Data* 1995, 40, 627-629.

[67] Hsu, C.-H.; Li, M.-H., *J. Chem. Eng. Data* 1997, 42, 502-507.

[68] Mandal, B.P.; Kundu, M.; Bandyopadhyay, S.S., *J. Chem. Eng. Data* 2003, 48, 703-707.

[69] Rinker, E.B.; Oelschlager, D.W.; Colussi, A.T.; Henry, K.R.; Sandall, O.C., *J. Chem. Eng. Data* 1994, 39, 392-395.

[70] Teng, T.T.; Maham, Y.; Hepler, L.G.; Mather, A.E., *Can. J. Chem. Eng.* 1994, 72, 125-129.

[71] Aguila-Hernández, J.; Gómez-Quintana, R.; Murrieta-Guevara, F.; Romero-Martinez, A.; Trejo, A., *J. Chem. Eng. Data* 2001, 46, 861-867.

[72] Welsh, L.M.; Davis, R.A., *J. Chem. Eng. Data* 1995, 40, 257-259.

[73] Hsu, C.-H.; Li, M.-H., *J. Chem. Eng. Data* 1997, 42, 714-720.

[74] Chenlo, F.; Moreira, R.; Pereira, G.; Vázquez, M.J.; Santiago, E., *J. Chem. Eng. Data* 2001, 46, 276-280.

[75] DiGuilio, R.M.; Lee, R.-J.; Shaeffer, S.T.; Brasher, L.L.; Teja, A.S., *J. Chem. Eng. Data* 1992, 37, 239-242.

[76] Maham, Y.; Teng, T.T.; Hepler, L.G.; Mather, A.E., *Can. J. Chem.* 1995, 73, 1514-1519.

[77] Al-Ghawas, H.A.; Hagewiesche, D.P.; Ruiz-Ibenez, G.; Sandall, O.C., *J. Chem. Eng. Data* 1989, 34, 385-391.

[78] Teng, T.T.; Maham, Y.; Hepler, L.G.; Mather, A.E., *J. Chem. Eng. Data* 1994, 39, 290-293.

[79] Paul, S.; Mandal, B., *J. Chem. Eng. Data* 2006, 51, 2242-2245.

[80] Haimour, N.; Sandall, O.C., *Chem. Eng. Sci.* 1984, 39, 1791-1796.

[81] Maham, Y.; Teng, T.T.; Hepler, L.G.; Mather, A.E., *J. Solution Chem.* 1994, 23, 195-205.

[82] Ma'mun, S.; Jakobsen, J.P.; Svendsen, H.F., *Ind. Eng. Chem. Res.* 2006, 45, 2505-2512.

[83] Al-Juaied, M.; Rochelle, G.T., *J. Chem. Eng. Data* 2006, 51, 708-717.

[84] Chauhan, R.K.; Yoon, S.J.; Lee, H.; Yoon, J.-H.; Shim, J.-G.; Song, G.-C.; Eum, H.-M., *Fluid Phase Equilib.* 2003, 208, 239-245.

[85] Pérez-Salado Kamps, A.; Xia, J.; Maurer, G., *AIChE Journal* 2003, 49, 2662-2670.

[86] Aroua, M.K.; Salleh, R.M., *Chem. Eng. Technol.* 2004, 27, 65-70.

[87] Jenab, M.H.; Abdi, M.A.; Najibi, S.H.; Vahidi, M.; Matin, N.S., *J. Chem. Eng. Data* 2005, 50, 583-586.

[88] Paul, S.; Mandal, B., *J. Chem. Eng. Data* 2006, 51, 1406-1410.

[89] Samanta, A.; Bandyopadhyay, S.S., *J. Chem. Eng. Data* 2006, 51, 467-470.

[90] Cullinane, J.T.; Rochelle, G.T., *Chem. Eng. Sci.* 2004, 59, 3619-3630.

[91] Dang, H.; Rochelle, G.T., *Sep. Sci. Technol.* 2003, 38, 337-357.

[92] Bishnoi, S.; Rochelle, G.T., *Chem. Eng. Sci.* 2002, 48, 2788-2799.

[93] Bishnoi, S.; Rochelle, G.T., *Chem. Eng. Sci.* 2000, 55, 5531-5543.

[94] Kundu, M.; Mandal, B.P.; Bandyopadhyay, S.S., *J. Chem. Eng. Data* 2003, 48, 789-796.

[95] Li, M.-H.; Chang, B.-C., *J. Chem. Eng. Data* 1994, 39, 448-452.

[96] Teng, T.T.; Mather, A.E., *J. Chem. Eng. Data* 1990, 35, 410-411.

[97] Teng, T.T.; Mather, A.E., *Can. J. Chem. Eng.* 1989, 67, 846-850.

[98] Xu, S.; Otto, F.D.; Mather, A.E., *J. Chem. Eng. Data* 1991, 36, 71-75.

[99] Mandal, B.P.; Bandyopadhyay, S.S., *Chemical Engineering Science* 2006, 61, 5440-5447.

[100] Chan, C; Maham, Y.; Mather, A.E.; Mathonat, C., *Fluid Phase Equilib.* 2002, 198, 239-250.

[101] Rebolledo-Libreros, M.E.; Trejo, A., *Fluid Phase Equilib.* 2004, 224, 83-88.

[102] Mandal, B.P.; Bandyopadhyay, S.S., *Chemical Engineering Science* 2005, 60, 6438-6451.

[103] Baek, J.-I.; Yoon, J.-H., *J. Chem. Eng. Data* 1998, 43, 635-637.

[104] Baek, J.-I.; Yoon, J.-H.; Eum, H.-M., *International Journal of Thermophysics* 2000, 21, 1175-1184.

[105] Yoon, S.J.; Lee, H.-S.; Lee, H.; Baek, J.-I.; Yoon, J.-H.; Eum, H.-M., *J. Chem. Eng. Data*, 2002, 47, 30-32.

[106] Kent, R.L.; Eisenberg, B., *Hydrocarbon Process.* 1976, 55, 87-90.

[107] Deshmukh, R.D.; Mather, A.E., *Chem. Eng. Sci.* 1981, 36, 355-362.

[108] Pitzer, K.S., *J. Phys. Chem.* 1973, 77, 268-277.

[109] Clegg, S.L.; Pitzer, K.S., *J. Phys. Chem.* 1992, 96, 3513-3529.

[110] Austgen, D.M., "A Model for Vapor-Liquid Equilibrium for Acid Gas-Alkanolamine-Water Systems", Ph.D. thesis, The University of Texas at Austin, Austin, TX, USA, 1989.

[111] Posey, M.L., "Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions", Ph.D. thesis, The University of Texas at Austin, Austin, TX, USA, 1996.

[112] Bishnoi, S.; Rochelle, G.T., *Fluid Phase Equilib.* 2000, 168, 241-258.

[113] Vrachnos, A.; Kontogeorgis, G.; Voutsas, E., *Ind. Eng. Chem. Res.* 2006, 45, 5148-5154.

[114] Vrachnos, A.; Voutsas, E.; Magoulas, K.; Lygeros, A., *Ind Eng. Chem. Res.* 2004, 43, 2798-2804.

[115] Belzil, A.; Parent, C., *Biochem. Cell Biol.* 2005, 83, 70-77.

CHAPTER 1. Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-hydroxymethyl-1,3-propanediol

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Abstract/Résumé

The solubility of CO_2 in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) was measured for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at (283.15, 298.15 and 313.15) K and for CO_2 partial pressures within (2 to 75) kPa. These ranges were compatible with aqueous solutions in use in a CO_2 capture process using human carbonic anhydrase metalloenzyme. The influence of carbonic anhydrase on the solubility of CO_2 in AHPD solution with mass fraction of 2.5 % at (283.15, 298.15 and 313.15) K was also studied for CO_2 partial pressures below 9 kPa. The modified Kent-Eisenberg model was used to correlate the equilibrium solubility of CO_2 in aqueous AHPD solutions and to determine the deprotonation and carbamate stability constants for AHPD solutions. These equilibrium constants were expressed with temperature, amine concentration and CO_2 loading. To estimate the physical solubility of CO_2 in aqueous AHPD solutions, the solubility of N_2O in aqueous AHPD solutions was also measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K. It was found that the enzyme did not influence the solubility of CO_2 in these solutions as the enzyme's function is to catalyze the hydration of CO_2 without affecting the CO_2 thermodynamic equilibrium.

La solubilité du CO_2 dans des solutions aqueuses de 2-amino-2-hydroxyméthyle-1,3-propanediol (AHPD) a été mesurée pour des fractions massiques en AHPD dans les solutions de (0.15, 0.5, 1 et 2.5) % à (283.15, 298.15 et 313.15) K et pour des pressions partielles de CO_2 se situant entre (2 et 75) kPa. Ces conditions expérimentales sont compatibles avec celles d'un procédé pour la capture du CO_2 employant des solutions

aqueuses de AHPD et l'enzyme anhydrase carbonique humaine. L'influence de l'anhydrase carbonique sur la solubilité du CO_2 dans une solution aqueuse de AHPD ayant une fraction massique en AHPD de 2.5 % à (283.15, 298.15 et 313.15) K a aussi été étudiée pour des pressions partielles de CO_2 sous 9 kPa. Le modèle modifié de Kent-Eisenberg a été employé pour corréler la solubilité du CO_2 dans les solutions aqueuses de AHPD à l'équilibre et pour déterminer les constantes de déprotonation et de la stabilité du carbamate pour les solutions de AHPD. Ces constantes d'équilibre sont exprimées en fonction de la température, de la concentration d'amine et de la charge en CO_2 dans les solutions. Afin d'estimer la solubilité physique du CO_2 dans les solutions aqueuses de AHPD, la solubilité du N_2O dans les solutions aqueuses de AHPD a été mesurée dans les solutions ayant des fractions massiques en AHPD de (0.15, 0.5, 1, 2.5 et 10) % à (283.15, 298.15 et 313.15) K. Il a été déterminé que l'enzyme n'influence pas la solubilité du CO_2 dans ces solutions puisque la fonction de l'enzyme est de catalyser l'hydratation du CO_2 sans affecter l'équilibre thermodynamique du CO_2.

1.1 Introduction

Evidence that unaccountable consumption of fossil energy has deleterious repercussions on climate change is fostering the deployment of a wide portfolio of CO_2 capture concepts to preserve the "city rights", within the energy mix, of fossil energy resources, while ensuring capacious transition time for an implantation of cleaner energy alternatives. This is because the availability of fossil fuel resources and the ubiquity of their enabling infrastructures are anticipated to play a significant role in the world's energy mix into the upcoming decades. A thorough update and a critical review of such technology portfolio have been conducted in 2005 by the International Panel on Climate Change in its special report on carbon dioxide capture and storage.[1] A consensus emerged thereof that several newly proposed enabling above-ground processes for CO_2 capture still face interrogations regarding their engineering feasibility or economic viability within the context of mitigation of greenhouse gas emissions. Hence, the deployment of more efficient processes for the removal of carbon dioxide has become crucial, together with the development of new absorbents as one of urgent areas of research in addressing global-warming problems.

Recently, the use of aqueous solutions of sterically hindered amines has become of great interest as potential post-combustion CO_2 absorbents due to their high cyclic capacity, relatively high absorption rates at high CO_2 loadings, and loading capacities nearing up to 1 mol of CO_2/mol of amine in concentrated amine solutions. Due to the bulkiness of carbon groups attached to the amino group, the sterically hindered amines form unstable carbamates. Then, the carbamates hydrolysis forms bicarbonate and restores free amines that can react anew with additional carbon dioxide and allows absorption up to 1 mol of CO_2/mol of amine.[2] In the present work, aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), a primary sterically hindered amine, was examined as a potential CO_2 absorbent and buffering agent to be incorporated in an enzymatic CO_2 capture process involving the use of a zinc-bearing cytosolic metalloenzyme, namely type II human carbonic anhydrase.[3] Enzyme-enhanced biomimetic hydration of CO_2 into bicarbonates has been reported to outperform conventional OH⁻-mediated CO_2 chemical hydration and was originally proposed by Meldrum and Roughton.[4] More investigations on this topic were further carried out by different research groups[3,5-10] to promote CO_2 hydration into

bicarbonate ions according to the ping-pong catalytic mechanism explained by Silverman and Lindskog:[11]

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad (1.1)$$

$$CO_2(aq) + EZnOH^- + H_2O \rightleftharpoons EZnH_2O + HCO_3^- \qquad (1.2)$$

$$EZnH_2O + RNH_2 \rightleftharpoons EZnOH^- + RNH_3^+ \qquad (1.3)$$
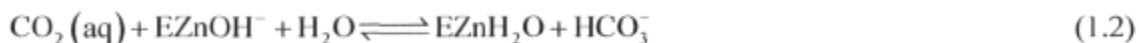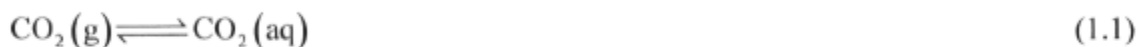
which implies a nucleophilic attack of (enzyme) zinc-bearing hydroxide on CO_2 (eq.1.2) and the regeneration of the active enzyme configuration through intermolecular proton transfer (eq.1.3) between the enzyme and the buffering amine molecule, here AHPD.

On the one hand, AHPD is used in the enzymatic process for CO_2 capture to slow down the pH fall off once protons are released subsequently to eq.1.2 step by activating the AHPD buffering function because pH is a key parameter for maintenance of an optimal enzyme activity.[11] Considering that the optimal pH value of aqueous AHPD solutions for the activity of the enzyme is around 8.5,[3] the concentrations of AHPD in aqueous solutions should therefore be controlled to keep the pH near this value.

On the other hand, the use of AHPD has also the advantage to increase the solubility of CO_2 in aqueous solutions according to the following chemical equilibria:

$$RNH_3^+ \xrightleftharpoons{K_1} H^+ + RNH_2 \qquad (1.4)$$

$$RNHCOO^- + H_2O \xrightleftharpoons{K_2} RNH_2 + HCO_3^- \qquad (1.5)$$

$$CO_2 + H_2O \xrightleftharpoons{K_3} H^+ + HCO_3^- \qquad (1.6)$$

$$HCO_3^- \xrightleftharpoons{K_4} H^+ + CO_3^{2-} \qquad (1.7)$$

$$H_2O \xrightleftharpoons{K_5} H^+ + OH^- \qquad (1.8)$$
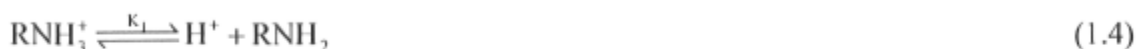
The chemical equilibrium in the systems consisting of CO_2, (primary or secondary) amines, and water is governed by the set of equations eqs.1.4-1.5 representing the amine protonation and carbamate hydrolysis, respectively, and eqs.1.6-1.8 which are typical ionization reactions for CO_2-containing aqueous systems.

New experimental data for CO_2 solubility in aqueous AHPD solutions for amine mass fractions of (0.15, 0.5, 1 and 2.5) % at (283.15, 298.15 and 313.15) K over CO_2 partial pressures ranging from (2 to 75) kPa are reported in this study. In addition, a 500 mg/L of human carbonic anhydrase was added in the aqueous AHPD solutions for an amine mass fraction of 2.5 % at (283.15, 298.15 and 313.15) K and CO_2 partial pressures below 9 kPa to verify the influence of the enzyme on the solubility of CO_2. For this system, the only available data are those by Park et al.[12,13] who reported the solubility data of carbon dioxide in aqueous (enzyme-free) AHPD for amine mass fractions of (10 and 20) % at (298.15, 313.15, 323.15 and 333.15) K over CO_2 partial pressures ranging from (1 to 2000) kPa. It is important to mention that the primary purpose of using AHPD in this study was not to exacerbate its carbonation/carbamation capability as sought with conventional hindered amines at *high* concentrations, but rather to provide a relatively amine-diluted aqueous medium for enabling the enzymatic hydration to proceed in an adequate manner. Another worth noting aspect is that the presence of enzyme in the AHPD dilute solutions will not displace the thermodynamic equilibrium reaction, once reached, as given by eqs.1.4-1.8. In other words, the carbonic anhydrase will accelerate the attainment of equilibrium and not the solution capacity for absorbing CO_2. This aspect will be discussed later based on the measured CO_2 solubilities.

For the analysis of the experimental data, and since CO_2 reacts in amine solutions, its physical solubility cannot be measured directly. As is widely accepted nowadays, nitrous oxide can be used as a non-reactive surrogate of CO_2 to estimate through N_2O analogy the physical solubility of CO_2 in amine solutions.[14-23] This analogy is subtended by the following Henry's law constant relationship:

$$\left(H_{CO_2} \right)_{amine} = \left(H_{N_2O} \right)_{amine} \left(\frac{H_{CO_2}}{H_{N_2O}} \right)_{water} \tag{1.9}$$

where $\left(H_{N_2O}\right)_{amine}$, $\left(H_{CO_2}\right)_{water}$ and $\left(H_{N_2O}\right)_{water}$ are respectively the Henry's law constants of N_2O in amine solution, and of CO_2 and N_2O in water. Versteeg and van Swaaij[14] proposed, on the basis of the available solubility data for N_2O and CO_2 in water, the following correlations for the solubility of N_2O and CO_2 in amine-free water:

$$H_{CO_2} / kPa \cdot m^3 \cdot kmol^{-1} = 2.8249 \times 10^6 \exp\left(-\frac{2044}{T/K}\right) \qquad (1.10)$$

$$H_{N_2O} / kPa \cdot m^3 \cdot kmol^{-1} = 8.5470 \times 10^6 \exp\left(-\frac{2284}{T/K}\right) \qquad (1.11)$$

In this work, the solubility of N_2O in aqueous AHPD solutions for amine mass fractions of (0.15, 0.5, 1, 2.5 and 10) % has been measured at (283.15, 298.15 and 313.15) K.

The equilibrium solubility of CO_2 in aqueous AHPD solutions was described on the basis of the model of Kent-Eisenberg.[24] This model was used to determine the deprotonation constant and carbamate stability constant for AHPD solutions expressed as functions of temperature, amine concentration and CO_2 loading.

In addition to the solubility measurements, new experimental data for the density and viscosity of the aqueous AHPD solutions for amine mass fractions of (0.15, 0.5, 1, 2.5 and 10) % and between (283.15 and 313.15) K are provided in this work. To our knowledge, no similar data of CO_2 and N_2O solubility data, density and viscosity are available in the open literature for the concentration and temperature ranges concerned by our study.

1.2 Experimental section

1.2.1 Materials

Aqueous AHPD solutions were prepared with double-distilled water and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) with a minimum purity of 99 % from Laboratoire MAT, Québec, Canada. All the chemicals were used without further purification. The carbon dioxide (CO_2) and nitrous oxide (N_2O) gases were of commercial grade with a

minimum purity of 99.9 % from Praxair, Québec, Canada. The enzyme human carbonic anhydrase was provided by CO_2 Solution Inc., Québec, Canada.

1.2.2 Density and viscosity measurements

Densities of aqueous AHPD solutions were measured by using a calibrated pycnometer having a bulb volume of 10 cm^3. Double-distilled water was used to determine the pycnometer volumes at various temperatures from (283.15 to 313.15) K. Density measurements were performed in a temperature-controlled water bath within ± 0.1 K. Temperature was measured with a calibrated mercury-filled glass-thermometer. A Mettler Toledo AB204 balance with a precision of ± 0.0001 g was used for preparing the solutions. All the measurements were performed at least in triplicate to verify the reproducibility of the results and to report averaged values. The uncertainty of the measured density was estimated to be within ± 0.3 $kg \cdot m^{-3}$.

Viscosities of aqueous AHPD solutions were measured with a glass capillary kinematic viscometer (Fisherbrand) having a capillary volume of 50 mL. Measurements were made in a water bath whose temperature was kept constant within ± 0.1 K. Kinematic viscosities were calculated from the efflux times measured with an electronic stopwatch with an accuracy of 0.01 s. All the measurements were performed at least thrice to verify the reproducibility of the results and to obtain averaged kinematic viscosities with reproducibility within ± 1.5 %. The dynamic viscosities were calculated by multiplying the kinematic viscosities with the corresponding solutions densities.

1.2.3 Solubility measurements

The setup used to measure the solubility of carbon dioxide (CO_2) and nitrous oxide (N_2O) is identical to the one employed in our group for previous solubility measurements.[25,26] It is illustrated in Figure A.1. A thorough description of the apparatus and the method used are presented elsewhere and will only be briefly summarized here.

The solubility setup is based on the saturation method and hence prevents uncertainties intrinsic to setups where gas and liquid phases have to be analyzed. The equilibrium cell consisted of a 250-mL flask wherein the magnetically-stirred amine-containing solutions

provide appropriate gas-liquid contacting. As the accuracy of the solubility measurements depends on accurate measurements of the total pressure inside the equilibrium cell, the gas pressure in the equilibrium cell was measured by means of a temperature-controlled MKS Baratron type 628B absolute pressure transducer (precision 0.25 % full scale, measurement resolution 0.001 % full scale). The Baratron transducer avoids vapor condensation during measurements and allows very accurate determinations of the total pressure. Both undissolved gas and solvent vapor pressures in the flask headspace were determined. The equilibrium cell together with its ancillary accessories were kept at a constant temperature using a thermostated bath controlled to within ± 0.01 K and the experimental uncertainty in the measured solubility was estimated to be about ± 1 %.

The solubility determination starts by preparing the aqueous AHPD solutions by weighing a quantity of amine and double-distilled water using a Mettler Toledo AB204 balance with a precision of ± 0.0001 g. To determine the volume of the liquid in the equilibrium cell, the density of the solutions in the temperature range and in the AHPD mass fraction range studied were required and measured as described previously.

A known solution volume was introduced into the equilibrium cell and the solution was allowed to slowly degas by liquid stirring under vacuum until the base pressure of the vacuum pump was reached. After completion of degassing, the equilibrium cell was sealed and temperature was assigned a set point T at which the solubility was to be measured. The vapor pressure P_{VS} of the gas-free solution was measured after the system had equilibrated. Gaseous carbon dioxide (or nitrous oxide) was added into a thermostated gas buret of volume V_{GB} maintained at temperature T_G, and the pressure P_{G1} was read. The number of moles n_{G1} of gas in the buret was computed as:

$$n_{G1} = \frac{P_{G1}V_{GB}}{RT_G} \tag{1.12}$$

After introducing a certain amount of gas into the equilibrium cell, a new pressure P_{G2} in the buret was read afresh, and the number of moles n_{G2} of gas left in the buret was recalculated:

$$n_{G2} = \frac{P_{G2}V_{GB}}{RT_G}$$ (1.13)

The difference n_{G1} - n_{G2} (= $n_{G,in}$) represents the number of moles of gas added to the equilibrium cell whose solution was vigorously stirred until reaching equilibrium as characterized by a constant pressure readout corresponding to the total (gas + solvent vapor) pressure. The gas partial pressure was determined after resting the solution vapor pressure P_{VS}. This allowed retrieving the number of moles $n_{G,fin}$ of gas left in the equilibrium cell headspace (eq.1.14) whereas the number of moles $n_{G,abs}$ of gas absorbed in the solution at equilibrium was determined according to eq.1.15:

$$n_{G,fin} = \left(P_{tot} - P_{VS}\right)\frac{V_{G,EC}}{RT}$$ (1.14)

$$n_{G,abs} = n_{G,in} - n_{G,fin}$$ (1.15)

The headspace volume of the equilibrium cell $V_{G,EC}$ is given by the difference between the cell geometrical volume V_{EC} and that occupied by the solution. All the runs were performed at least twice to ensure repeatability of the measurements which was fulfilled to within 1 %.

1.3 Thermodynamic model

Kent and Eisenberg[24] developed a simple thermodynamic model for predicting equilibrium data in amine-CO_2 systems using apparent equilibrium constants. The Kent-Eisenberg model was chosen for the base model because it yielded good performance for the correlation and prediction of CO_2 solubility in alkanolamine solutions in previous studies.[27-30] Besides, as long as computing time and convergence issues are considered, this simple model can be used more usefully than complex ones in actual absorption processes. The model is based *per se* on several equilibrium constants and the Henry's law relationship. The simplicity of Kent and Eisenberg model lies in the fact that only the equilibrium constants involving the target amine are determined by fitting the measured gas solubility data while using the carbonic acid and water equilibrium constants as well as

Henry's law constants. A more complete model was proposed by Deshmukh and Mather[31] to account for the activity coefficients and all possible ionic/nonionic species. However, it is very unlikely that the relatively low concentrations of amines employed in the present study justifies an as comprehensive and cumbersome model representation for the CO_2-AHPD systems being studied. Therefore, the equilibrium model developed in this study is based on a slight adaptation of the Kent and Eisenberg model and assumes that all activity coefficients and fugacity coefficients to be unity except for the species intervening in the amine-related apparent equilibrium K_1 and K_2 (see eqs.1.4,1.5). Hence, only these two constants are correlated as a function of temperature -as for true activity-based equilibrium constant-, and as a function of amine concentration and CO_2 loading as *ad hoc* and empirical approximations for the activity coefficient related constants. According to Li and Shen[29] this artifice consists in accounting for the non-ideality of the solution only via the set of amine-related constants.

The apparent equilibrium constants based on species concentrations and representing the reactions in the CO_2/amine/H_2O systems, enumerated above (eqs.1.4-1.8) in the Introduction section, are given by:

$$K_a = K_1 = \frac{[RNH_2][H^+]}{[RNH_3^+]} \tag{1.16}$$

$$K_c = \frac{1}{K_2} = \frac{[RNHCOO^-]}{[RNH_2][HCO_3^-]} \tag{1.17}$$

$$K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{1.18}$$

$$K_4 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{1.19}$$

$$K_5 = [H^+][OH^-] \tag{1.20}$$

In addition to the above equilibrium equations, overall species mole and charge balances must be satisfied. In these balance equations, m denotes the molarity of the AHPD solution and α denotes the CO_2 loading in the solutions expressed as total moles of CO_2 absorbed in the solutions (both chemically and physically) per mole of amine.

$$m = [RNH_2] + [RNHCOO^-] + [RNH_3^+] \tag{1.21}$$

$$m\alpha = [RNHCOO^-] + [HCO_3^-] + [CO_3^{2-}] + [CO_2] \tag{1.22}$$

$$[H^+] + [RNH_3^+] = [RNHCOO^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \tag{1.23}$$

The CO_2 equilibrium partial pressure is related to the physically dissolved CO_2 concentration in the solution by means of Henry's law:

$$P_{CO_2} = H_{CO_2}[CO_2] \tag{1.24}$$

Where, P_{CO_2} and H_{CO_2} denote the equilibrium partial pressure of carbon dioxide in the gas phase and Henry's law constant, respectively.

Eight independent equations (eqs.1.16-1.23) are used to calculate the concentrations of the eight species, i.e., $[RNH_2]$, $[RNH_3^+]$, $[RNHCOO^-]$, $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$, $[OH^-]$. Eq.1.24 is used to calculate the equilibrium partial pressure of CO_2 from the $[CO_2]$ determined by the model. The values of H_{CO_2} were estimated from the solubility of N_2O in aqueous solutions of AHPD for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K. The values of the equilibrium constant K_3, K_4 and K_5 were taken from the literature as in the model of Kent and Eisenberg and are summarized in Table 1.1. The amine deprotonation constant K_a and the carbamate stability constant K_c were determined by forcing a fit with the experimental solubility data. To solve the system of nonlinear algebraic equations, initial estimates of the concentrations had to be provided. The following initial estimates were provided, and the Newton's method was used:

$$[RNHCOO^-] = 1.0E - 10 \tag{1.25}$$

$$[RNH_2] = m - (m\alpha - P_{CO_2} / H_{CO_2}) \tag{1.26}$$

$$[RNH_3^+] = m\alpha - P_{CO2} / H_{CO_2} \tag{1.27}$$

$$[HCO_3^-] = m\alpha - P_{CO_2} / H_{CO_2} \tag{1.28}$$

$$[CO_2] = P_{CO_2} / H_{CO_2} \tag{1.29}$$

$$[H^+] = [OH^-] = 1.0E - 7 \tag{1.30}$$

$$[CO_3^{2-}] = 1.0E - 4 \tag{1.31}$$

Numerical values for K_a and K_c were determined using the Levenberg-Marquardt algorithm that minimizes the difference between the measured values of equilibrium CO_2 partial pressures and the values calculated from the model. The objective function was the sum of the N individual discrepancy terms:

$$F = \sum_{i=1}^{N} \frac{\left(P_{CO_2}\right)_i^{exp} - \left(P_{CO_2}\right)_i^{cal}}{\left(P_{CO_2}\right)_i^{exp}} \tag{1.32}$$

Table 1.1. Equilibrium Constants

Equilibrium constant[a]	A	$B \times 10^{-4}$	$C \times 10^{-8}$	$D \times 10^{-11}$	$E \times 10^{-13}$
K_3 (mol/L)	-241.818	29.8253	-1.48528	0.332648	-0.282393
K_4 (mol/L)	-294.74	36.4385	-1.84158	0.415793	-0.354291
K_5 [(mol/L)^2]	39.5554	-9.879	0.568827	-0.146451	0.136146

[a] $K_i = \exp[A + B/T + C/T^2 + D/T^3 + E/T^4]$

1.4 Results and discussion

1.4.1 Density and viscosity

Densities of aqueous AHPD solutions were measured over the temperature range from (283.15 to 313.15) K and at the AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % and

2.5 % with an enzyme concentration of 500 mg/L. The experimental results are presented in Table 1.2. In addition, the influence of temperature and AHPD concentrations is illustrated in Figure 1.1, along with the density of an aqueous solution of AHPD mass fraction of 10 % at (303.15 and 313.15) K reported by Park et al.[12] It can be seen that densities of the aqueous AHPD solutions decrease with increasing temperature and decreasing AHPD concentrations. Furthermore, an enzyme concentration of 500 mg/L brought about *circa* 0.015 % change in the density value and thus had barely influenced the density of the aqueous solution of AHPD mass fraction of 2.5 %. As shown in Figure 1.1, the density of the aqueous solution of AHPD mass fraction of 10 % at (303.15 and 313.15) K is in excellent agreement with the results presented by Park et al.[12] The average absolute deviation (AAD) is 0.025 %.

Table 1.2. Densities (ρ/kg·m^{-3}) of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions

T/K	mass fraction of AHPD/%					
	0.15	0.5	1	2.5	2.5+ enzyme[a]	10
283.15	1000.5	1001.6	1002.4	1006.8	1007.0	1026.2
288.15	999.9	1001.3	1001.8	1006.0	1006.0	1025.0
293.15	999.1	1000.5	1001.0	1005.1	1004.9	1023.8
298.15	997.9	999.4	1000.0	1003.8	1003.6	1022.4
303.15	996.6	997.8	998.7	1002.3	1002.2	1020.8
308.15	995.0	996.0	997.2	1000.7	1000.6	1019.4
313.15	993.1	993.6	995.4	998.7	998.9	1017.7

[a](Free) carbonic anhydrase II concentration = 500 mg/L
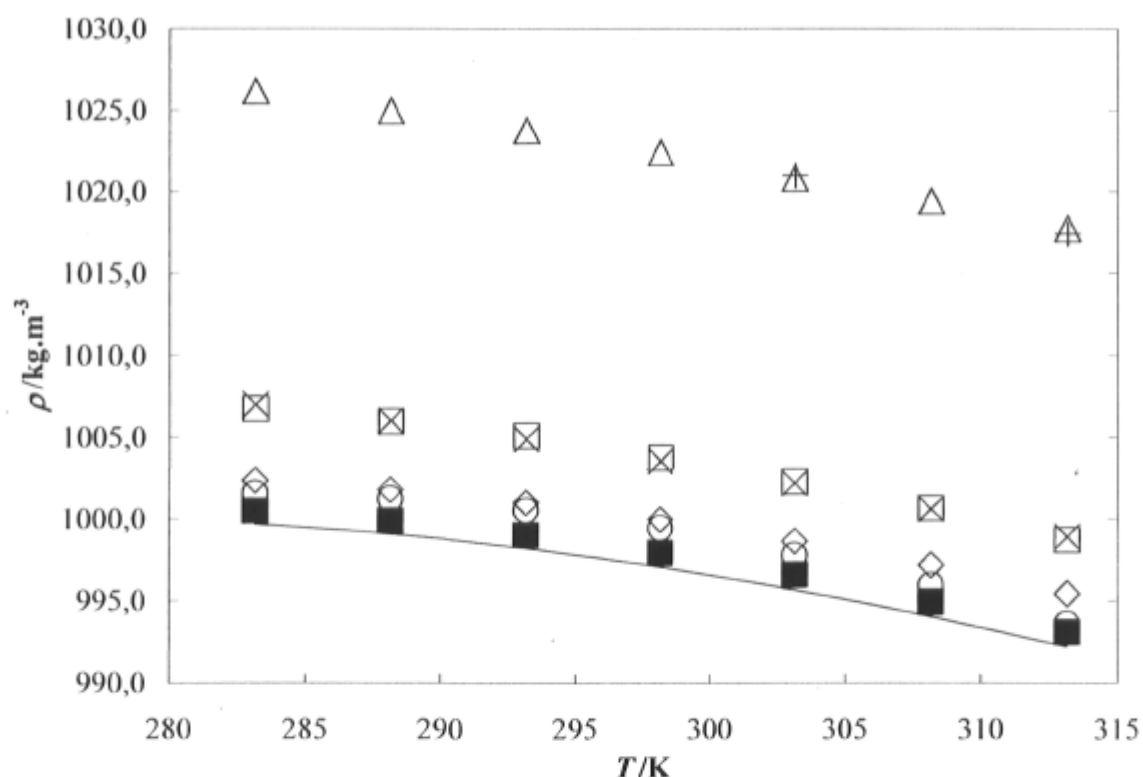
Figure 1.1. Densities (ρ/kg·m^{-3}) of aqueous AHPD solutions (AHPD mass fraction %): ■, 0.15; ○, 0.5; ◊, 1; □, 2.5; ×, 2.5 with an enzyme concentration of 500 mg/L; △, 10; +, Park et al.[12] Solid line shows trend for water density.

Viscosities of aqueous AHPD solutions were measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % and 2.5 % with an enzyme concentration of 500 mg/L at (283.15, 298.15 and 313.15) K. The experimental results of dynamic viscosities are presented in Table 1.3. In addition, the influence of temperature and AHPD concentrations on the viscosities of the solutions is illustrated in Figure 1.2, along with the viscosity of an aqueous solution of AHPD mass fraction of 10 % at 313.15 K reported by Park et al.[12] It can be seen that viscosities of aqueous AHPD solutions increase with decreasing temperature and increasing AHPD concentrations. Although the viscosity of the aqueous solution of AHPD mass fraction of 2.5 % with an enzyme concentration of 500 mg/L was slightly higher than the viscosity of the corresponding enzyme-free AHPD solution, the presence of the enzyme at the chosen concentration barely increased the solution viscosity by *circa* 0.3 % which can safely be ignored an increment. The viscosity of the aqueous

solution of AHPD mass fraction of 10 % is significantly higher than the viscosity of the aqueous solution of AHPD mass fraction of 2.5 %, besides the viscosity of the AHPD mass fraction of 10 % aqueous solution at 313.15 K is in excellent agreement with the result presented by Park et al.[12] The AAD was found to be only 1.3 %.

Table 1.3. Viscosities (η/mPa·s) of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions

T/K	mass fraction of AHPD/%					
	0.15	0.5	1	2.5	2.5+ enzyme[a]	10
283.15	1.315	1.354	1.360	1.422	1.427	1.802
298.15	0.905	0.913	0.917	0.959	0.961	1.173
313.15	0.656	0.662	0.669	0.696	0.699	0.857

[a](Free) carbonic anhydrase II concentration = 500 mg/L
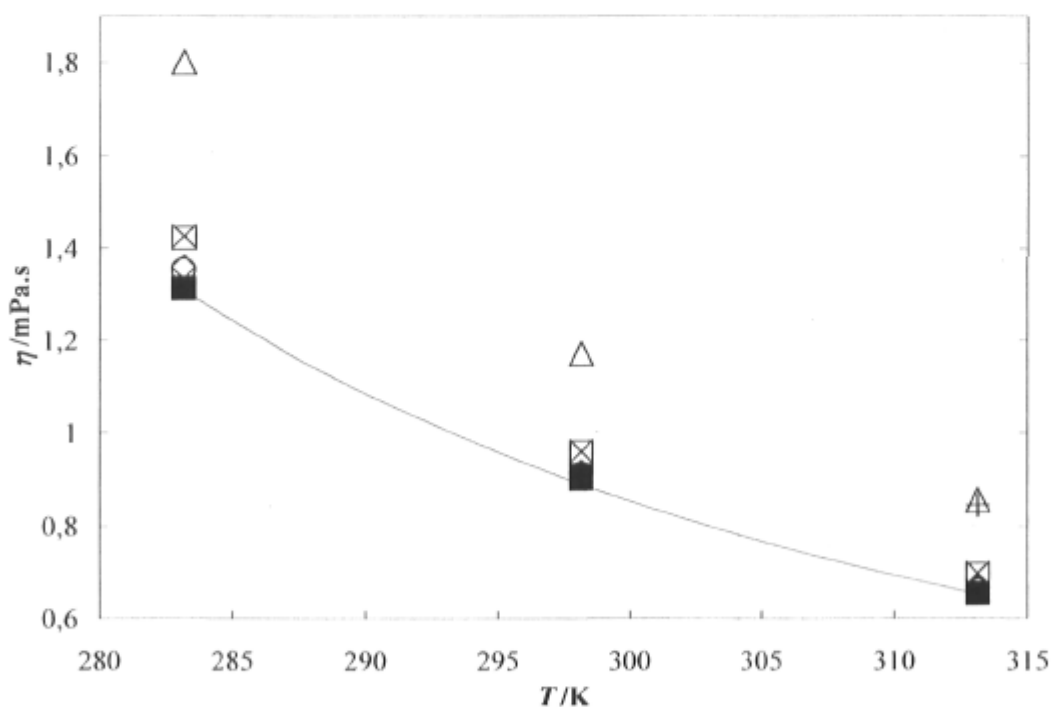
Figure 1.2. Viscosities (η/mPa·s) of aqueous AHPD solutions (AHPD mass fraction %): ■, 0.15; ○, 0.5; ◊, 1; □, 2.5; ×, 2.5 with an enzyme concentration of 500 mg/L; Δ, 10; +, Park et al.[12]. Solid line shows trend for water dynamic viscosity.

1.4.2 Solubility of CO_2 and N_2O in water and physical solubilities in aqueous AHPD solutions

In order to validate the solubility apparatus and the experimental procedure, the solubilities of CO_2 and N_2O in water at (283.15, 288.15, 298.15 and 313.15) K were measured and compared with those reported in the literature.[14,18,32] Data expressed in term of Henry's law constants are presented in Table 1.4 and illustrated in Figures 1.3 and 1.4, in comparison with the literature data. The results of this study are generally in good agreement with the literature results. Eq.1.10 appears to be an accurate correlation for the solubility of CO_2 in water as a function of temperature as confirmed by Figure 1.3. The AADs are (0.73, 2.33 and 0.58) % with respect to the results of Versteeg and van Swaaij[14], Saha et al.[18] and Al-Ghawas et al.[32], respectively. The solubilities of N_2O in water agree well with those reported by Versteeg and van Swaaij[14] and Saha et al.[18] However, data reported by Al-Ghawas et al.[32] are not in good agreement on the whole temperature range investigated. Eq.1.11 appears to be accurate for the solubility of N_2O in water as a function of temperature for the results in this study and those by Versteeg and van Swaaij[14] and Saha et al.[18] as shown in Figure 1.4. The AADs are (2.03, 0.80 and 9.16) % with respect to the results of Versteeg and van Swaaij[14], Saha et al.[18] and Al-Ghawas et al.[32], respectively.

Table 1.4. Solubility of CO_2 and N_2O in Water and Comparison with Literature Values

	T/K	H/(kPa·m³·kmol⁻¹)	% deviationᵃ	ref
CO_2	283.15	1941	–	this study
	288.15	2360	4.39	Saha et al.[18]
		2240	0.74	Al-Ghawas et al.[32]
		2257	–	this study
	298.15	2967	1.15	Versteeg and van Swaaij[14]
		2993	0.28	Saha et al.[18]
		2984	0.59	Al-Ghawas et al.[32]
		3002	–	this study

	313.15	4219	0.31	Versteeg and van Swaaij[14]
		4250	0.40	Al-Ghawas et al.[32]
		4233	-	this study
N_2O	283.15	2590	-	this study
	288.15	3107	1.28	Saha et al.[18]
		2897	5.89	Al-Ghawas et al.[32]
		3068	-	this study
	298.15	4132	0.61	Versteeg and van Swaaij[14]
		4120	0.32	Saha et al.[18]
		3910	5.03	Al-Ghawas et al.[32]
		4107	-	this study
	313.15	6061	3.45	Versteeg and van Swaaij[14]
		5021	16.6	Al-Ghawas et al.[32]
		5852	-	this study

[a]Percentage deviation expressed as absolute relative difference between Henry's constants from literature and as measured in present study
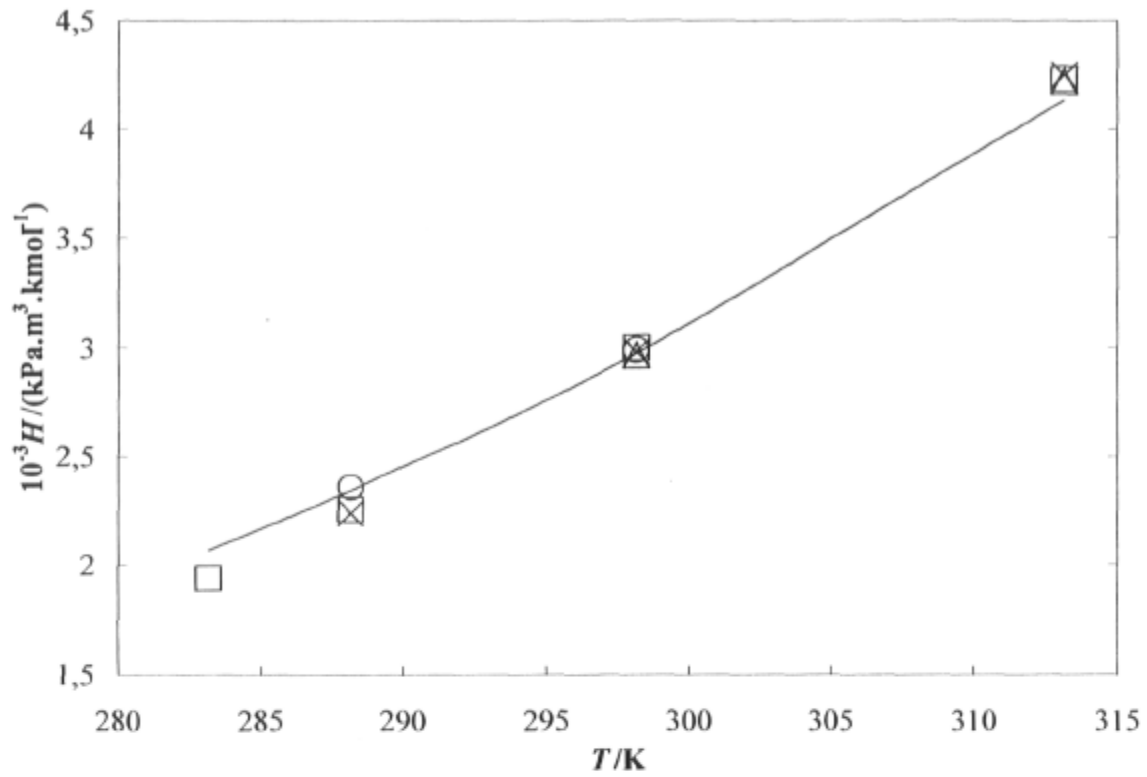
Figure 1.3. Henry's constant of CO_2 in water (H) as function of temperature: □, this study; Δ, Versteeg and van Swaaij[14]; ○, Saha et al.[18]; ×, Al-Ghawas et al.[32]; Line calculated using eq. 10.
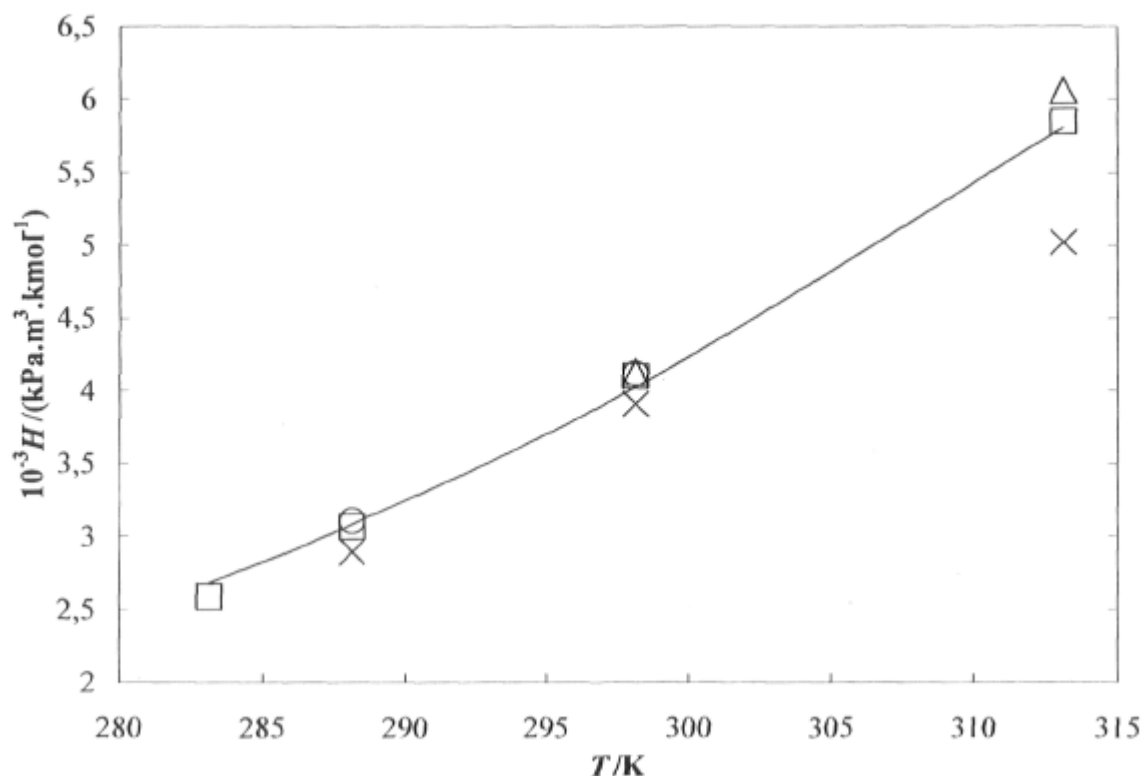
Figure 1.4. Henry's constant of N_2O in water (H) as function of temperature: □, this study; Δ, Versteeg and van Swaaij[14]; ○, Saha et al.[18]; ×, Al-Ghawas et al.[32]; Line calculated using eq.11.

The solubilities of N_2O in aqueous AHPD solutions were measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K. The results are expressed in terms of Henry's law constants and are presented in Table 1.5 along with the estimated physical solubilities of CO_2 in aqueous AHPD solutions using eq. 1.9. The solubilities of N_2O and CO_2 decrease with increasing either temperature for given solution amine concentration or concentration of AHPD in aqueous solutions at constant temperature. Fractions of estimated physical concentrations of CO_2 $\left(C_{CO_2 phys.}\right)$/total concentrations of CO_2 in the aqueous AHPD solutions for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at 283.15 K are also presented in APPENDIX B, Table B.1. As expected, the fractions increase with increasing CO_2 partial pressures since the physical solubility of CO_2 in the aqueous solutions is directly proportional to the partial pressure of CO_2 by Henry's law. Fractions of estimated physical concentrations of CO_2/total concentrations of

CO_2 in the aqueous AHPD solutions decrease with increasing AHPD mass fractions. As expected, an increase in AHPD mass fractions enhances the solubility of CO_2 and reduces the physical solubility of CO_2 in the aqueous AHPD solutions.

Table 1.5. Experimental Henry's Constant for N_2O, H_{N_2O}, and Estimated Henry's Constant for CO_2, H_{CO_2}, in Aqueous AHPD Solutions for AHPD Mass Fractions from (0.15 to 10) % and for Temperatures from (283.15 to 313.15) K

AHPD mass fraction %	T/K			T/K		
	283.15	298.15	313.15	283.15	298.15	313.15
	H_{N_2O}/(kPa·m^3·kmol^{-1})			H_{CO_2}/(kPa·m^3·kmol^{-1})		
0.15	2580	4114	5864	1934	3007	4242
0.5	2597	4127	5885	1947	3017	4257
1	2604	4129	5893	1952	3018	4262
2.5	2616	4161	5909	1961	3041	4274
10	2785	4345	6171	2087	3176	4463

1.4.3 Solubility of CO_2 in aqueous AHPD solutions and the correlation

The solubilities of CO_2 in aqueous AHPD solutions were measured for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at (283.15, 298.15 and 313.15) K over CO_2 partial pressures ranging from 2 to 75 kPa and for an AHPD mass fraction of 2.5 % aqueous solution with an enzyme concentration of 500 mg/L at (283.15, 298.15 and 313.15) K for CO_2 partial pressures below 9 kPa. The experimental solubility data are presented in Table 1.6 and are expressed as moles per Liter of CO_2 (*i.e.*, total or chemically plus physically) absorbed in the AHPD solutions. In addition, the influence of AHPD concentrations on the solubilities of CO_2 in aqueous solutions at (298.15 and 313.15) K is illustrated in Figures 1.5a,b. The influence of AHPD concentrations on the solubilities of CO_2 in aqueous solutions at (283.15 K) is also illustrated in APPENDIX C, Figure C.1. At a constant temperature and for a given equilibrium CO_2 partial pressure, the solubilities of CO_2 increase with increasing AHPD concentrations of the solutions. Moreover, Figure 1.6 shows the influence of temperature on the solubilities of CO_2 in aqueous solution of AHPD

mass fraction of 2.5 %. The influence of temperature on the solubilities of CO_2 in aqueous solution of AHPD mass fraction of 0.15 % is also shown in APPENDIX C, Figure C.2. The solubilities of CO_2 in aqueous AHPD solutions decrease, as expected, with an increase in temperature. The CO_2 partial pressure and corresponding solubility of carbon dioxide in the presence of carbonic anhydrase is also shown in Figure 1.6 in the aqueous solution of AHPD mass fraction of 2.5 %. As expected, the presence of enzyme did not affect the position of the equilibrium points on the isotherms considering, on the one hand that, the salting in/out effects contributed by 500 mg/L enzyme concentration were by and large marginal. On the other hand, since the enzyme is sought to act like a biomimetic catalyst, it must go unnoticed in terms of the thermodynamics of the carbon dioxide, carbonate/bicarbonate, and carbamate system. However, it was experimentally observed that introduction of the enzyme in the equilibrium cell enabled a noticeable acceleration towards the attainment of equilibrium by the system. It was also observed that the influence of CO_2 partial pressure on the solubility of CO_2 in aqueous AHPD solutions seems to increase with decreasing AHPD concentrations of the solutions, especially when the AHPD mass fraction of the solution is 0.15 %. As AHPD concentration of the solutions decreases, the tendency of the CO_2 solubility becomes somewhat similar to that in physical solvents since the concentrations of AHPD of the solutions are low. For a physical solvent, the CO_2 solubility increases relatively slowly with relatively rapidly increasing CO_2 partial pressure since the solubility is directly related to the CO_2 partial pressure via Henry's law.

The solubilities of CO_2 in aqueous AHPD solutions for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at (283.15, 298.15 and 313.15) K over CO_2 partial pressures ranging from 2 to 75 kPa were used to determine the deprotonation constant and the carbamate stability constant. The deprotonation constant K_a and the carbamate stability constant K_c are assumed to be functions of temperature, initial amine concentration (m in mol/L), and CO_2 loading (α). Note that the CO_2 loading is defined as usual as the ratio between the mole concentration of (total) CO_2 (*i.e.*, chemically plus physically absorbed) to the initial mole concentration of the amine, $\alpha = \{[RNHCOO^-]+[CO_2]+[HCO_3^-]+[CO_3^{2-}]\}/m$. Using the least-squares fit to the equilibrium partial pressure data of CO_2 in aqueous AHPD solutions, the equilibrium constants were determined as follows:

$$K_a = \exp\left[13.5 - 12.7 \times 10^3/T + 2.00 \times 10^8/T^3 + 2.25\alpha - 3.60/\alpha - 2.250/\alpha^2 + 0.033 \times \ln(m)\right]$$
(1.33)

$$K_c = \exp\left[6.51 - 7.58 \times 10^3/T + 3.78 \times 10^8/T^3 - 0.60\alpha + 3.88/\alpha - 0.985/\alpha^2 + 0.986 \times \ln(m)\right]$$
(1.34)

Numerical values of K_a and K_c in function of temperature (T), CO_2 loading (α) and initial amine concentration (m) are presented in APPENDIX D, Table D.1. Figures 1.5a,b and 1.6 show comparisons between calculated and experimental results. It can be seen from these figures that the curves of partial pressures of CO_2, calculated from the equilibrium model, are in good agreement with the experimental partial pressures of CO_2. The absolute average deviation (AAD) between calculated and experimental results is only of 1.55 % whereas the deviations between the calculated and experimental results were between (0.0164 to 7.07) % confirming the adequacy of the Kent and Eisenberg[24] variant model used here to fit the CO_2 solubility data in dilute AHPD aqueous solutions with and without free type II human carbonic anhydrase.

Table 1.6. Solubility of CO_2 in Aqueous AHPD Solutions for AHPD Mass Fractions from (0.15 to 2.5) % and for Temperatures from (283.15 to 313.15) K

283.15 K									
0.15 %		0.5 %		1 %		2.5 %		2.5 % with enzyme[a]	
P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]
3.19	1.33	4.25	3.84	3.65	6.72	2.98	13.44	3.07	13.68
5.35	1.46	10.1	4.33	9.18	7.65	7.29	16.45	8.16	16.75
12.0	1.85	22.3	5.02	15.7	8.24	15.4	18.44		
25.9	2.58	44.8	6.15	23.1	8.69	27.7	19.65		
43.2	3.42	67.7	7.25	47.7	10.09	49.3	21.39		
61.9	4.30	68.7	7.34	74.1	11.29	69.7	22.26		
64.0	4.48								
68.8	4.68								

298.15 K									
0.15 %		0.5 %		1 %		2.5 %		2.5 % with enzyme[a]	
P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]
2.04	1.04	3.83	3.11	3.32	5.03	2.89	9.25	2.93	9.31
8.48	1.43	6.37.	3.50	4.53	5.57	6.80	12.53	7.44	12.68
13.4	1.62	10.2	3.82	6.33	6.04	11.3	14.43		
29.6	2.19	23.7	4.55	7.34	6.26	21.7	16.59		
38.0	2.48	47.8	5.35	12.93	7.02	53.5	19.24		
47.9	2.80	73.1	6.16	20.92	7.67	72.0	19.94		
68.9	3.47			48.76	9.05				
70.2	3.49			72.96	9.85				

313.15 K									
0.15 %		0.5 %		1 %		2.5 %		2.5 % with enzyme[a]	
P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]	P_{CO_2}	$10^2 C_{CO_2}$[b]
1.91	0.75	2.73	1.93	2.26	2.91	3.77	6.54	4.05	6.62
5.62	1.08	5.88	2.57	6.15	4.32	4.91	7.34	4.99	7.34
10.8	1.29	11.4	3.18	12.2	5.47	6.69	8.48		
27.1	1.79	25.8	3.96	20.7	6.33	13.9	10.97		
37.9	2.06	49.2	4.69	49.7	7.80	29.7	13.97		
48.3	2.31	73.6	5.29	74.0	8.49	51.8	16.08		
71.8	2.81					74.8	16.85		
73.4	2.83								

[a](Free) carbonic anhydrase II concentration = 500 mg/L

[b]$C_{CO_2} = [RNHCOO^-] + [CO_2] + [HCO_3^-] + [CO_3^{2-}]$ expressed in $mol \cdot L^{-1}$
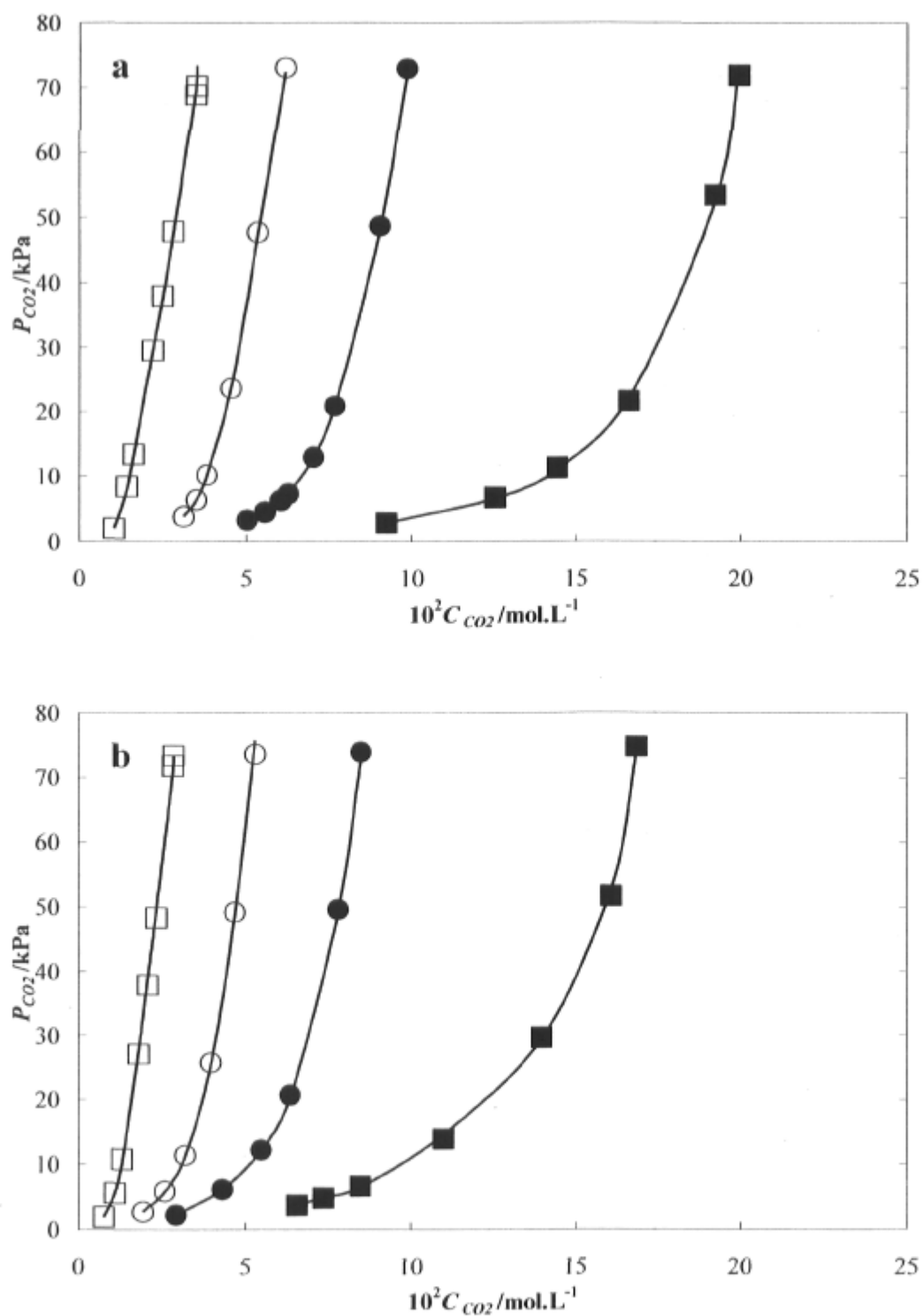
Figure 1.5. Solubilities of carbon dioxide in aqueous AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % solutions at (a) 298.15 K, (b) 313.15 K: □, 0.15; ○, 0.5; ●, 1; ■, 2.5. Lines calculated by the thermodynamic model.
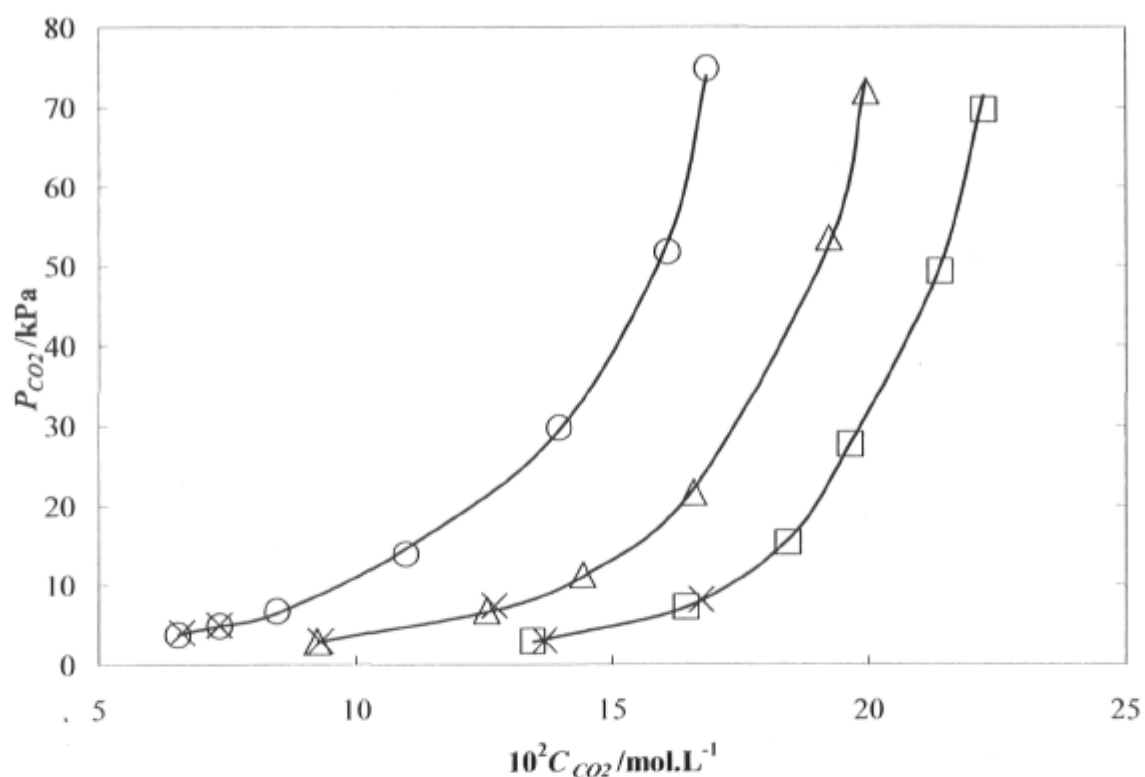
Figure 1.6. Solubilities of carbon dioxide in an aqueous AHPD mass fraction of 2.5 % solution at various temperatures: $\square$, 283.15 K; $\triangle$, 298.15 K; $\circ$, 313.15 K; $\times$, solubilities of carbon dioxide in an aqueous AHPD mass fraction of 2.5 % solution with an enzyme concentration of 500 mg/L at various temperatures. Lines calculated by the thermodynamic model.

1.5 Conclusion

In this work, aqueous 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) was studied as potential carbon dioxide capture solutions for an enzymatic process relying on type II human carbonic anhydrase. The densities and viscosities of aqueous AHPD solutions were measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K and for an aqueous solution of AHPD mass fraction of 2.5 % with an enzyme concentration of 500 mg/L at (283.15, 298.15 and 313.15) K. The density of aqueous AHPD solutions were also measured at (288.15, 293.15, 303.15 and 308.15) K. The solubility of N_2O in aqueous AHPD solutions was measured for AHPD mass fractions of

(0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K and was used to estimate the physical solubility of CO_2 in aqueous AHPD solutions. In addition, the solubility of CO_2 in aqueous AHPD solutions was measured for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) mass % at (283.15, 298.15 and 313.15) K and for CO_2 partial pressures ranging from (2 to 75) kPa. The modified Kent-Eisenberg model was used to correlate the equilibrium solubility of carbon dioxide in aqueous AHPD solutions and to determine the deprotonation constant K_a and carbamate stability constant K_c for AHPD solutions. There was a good agreement between the experimental results and those calculated from the equilibrium model. The chemical equilibrium constants are expressed as functions of temperature, amine concentration (m in mol/L) and carbon dioxide loading (α). The influence of the presence of enzyme on the solubility of CO_2 in an aqueous solution of 2.5 mass % AHPD at (283.15, 298.15 and 313.15) K was also studied for CO_2 partial pressures below 9 kPa. It was found that the enzyme does not seem to affect the solubility of CO_2 in these solutions as the enzyme's function is to catalyze the hydration of CO_2 without changing in any meaningful manner the CO_2 solubility as dictated by thermodynamics.

Acknowledgment

1.6 References

(1)   IPCC *Special report on carbon dioxide capture and storage* (http://arch.rivm.nl/env/int/ipcc), Chapter III: Capture, 2005

(2)   Sartori, G.; Savage, D. W. Sterically Hindered Amines for CO_2 Removal from Gases. *Ind. Eng. Chem. Fundam.* **1983**, 22, 239-249.

(3)   Belzil, A.; Parent, C. Méthodes de qualification des immobilisations chimiques d'une enzyme sur un support solide. *Biochem. Cell Biol.* **2005**, 83, 70-77.

(4)   Meldrum, N. U.; Roughton, F. J. W. Carbonic Anhydrase: its Preparation and Properties. *J. Physiol.* **1933**, 80, 113-141.

(5) Bond, G. M.; Stringer, J.; Brandvold, D. K.; Simsek, F. A.; Medina, M. G.; Egeland, G. Development of Integrated System for Biomimetic CO_2 Sequestration Using the Enzyme Carbonic Anhydrase. *Energy Fuels* **2001**, 15, 309-316.

(6) Jiang, Z.; Wu, H., Xu, S.; Huang, S. Enzymatic Conversion of Carbon Dioxide to Methanol by Dehydrogenases Encapsulated in Sol-Gel Matrix. *Fuel Chem. Div. Preprints* **2002**, 47, 306.

(7) Trachtenberg, M. C.; Ge, J. Enzyme-Based Hollow Fiber Contained Liquid Membrane for CO_2 Removal. *AIChE Conferences*, New-Orleans, Louisianne, March 10-14th 2002. AIChE Customer Service, New York, **2001**.

(8) Mirjafari, P.; Asghari, K.; Mahinpey, N. Investigating the Application of Enzyme Carbonic Anhydrase for CO_2 Sequestration Purposes. *Ind. Eng. Chem. Res.* **2007**, 46, 921-926.

(9) Bhattacharya, S.; Nayak, A.; Schiavone, M.; Bhattacharya, S. K. Solubilization and Concentration of Carbon Dioxide: Novel Spray Reactors with Immobilized Carbonic Anhydrase. *Biotechnol. Bioeng.* **2004**, 86, 37-46.

(10) Blais, R.; Rogers, P. Process and apparatus for the treatment of carbon dioxide with carbonic anhydrase. US Patent 6,524,843, CO_2 Solution Inc., **2003**.

(11) Silverman, D. N.; Lindskog, S. The Catalytic Mechanism of Carbonic Anhydrase: Implications of a Rate-Limiting Protolysis of Water, *Acc. Chem. Res.* **1988**, 21, 30-36.

(12) Park, J.-Y.; Yoon, S. J.; Lee, H.; Yoon, J.-H.; Shim, J.-G.; Lee, J. K.; Min, B.-Y.; Eum, H.-M. Density, Viscosity, and Solubility of CO_2 in Aqueous Solutions of 2-Amino-2-hydroxymethyl-1,3-propanediol. *J. Chem. Eng. Data* **2002**, 47, 970-973.

(13) Park, J.-Y.; Yoon, S. J.; Lee, H. Effect of Steric Hindrance on Carbon Dioxide Absorption into New Amine Solutions: Thermodynamic and Spectroscopic Verification through Solubility and NMR Analysis. *Environ. Sci. Technol.* **2003**, 37, 1670-1675.

(14) Versteeg, G.F.; van Swaaij, W. P. M. Solubility and Diffusivity of Acid Gases (CO_2, H_2S) in Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data* **1988**, 33, 29-34.

(15) Mandal, B. P.; Kundu, M.; Bandyopadhyay, S. S. Physical Solubility and Diffusivity of N_2O and CO_2 into Aqueous Solutions of (2-Amino-2-methyl-1-propanol + Monoethanolamine) and (*N*-methyldiethanolamine + Monoethanolamine). *J. Chem. Eng. Data* **2005**, 50, 352-358.

(16) Mandal, B. P.; Kundu, M.; Padhiyar, N. U.; Bandyopadhyay, S. S. Physical Solubility and Diffusivity of N_2O and CO_2 into Aqueous Solutions of (2-Amino-2-methyl-1-propanol + Diethanolamine) and (*N*-methyldiethanolamine + Diethanolamine). *J. Chem. Eng. Data* **2004**, 49, 264-270.

(17) Xu, S.; Otto, F. D.; Mather, A. E. Physical Properties of Aqueous AMP Solutions. *J. Chem. Eng. Data* **1991**, 36, 71-75.

(18) Saha, A. K.; Bandyopadhyay, S. S.; Biswas, A. K. Solubility and Diffusivity of N_2O and CO_2 in Aqueous Solutions of 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1993**, 38, 78-82.

(19) Tsai, T.-C.; Ko, J.-J.; Wang, H.-M.; Lin, C.-Y.; Li, M.-H. Solubility of Nitrous Oxide in Alkanolamine Aqueous Solutions. *J. Chem. Eng. Data* **2000**, 45, 341-347.

(20) Li, M.-H.; Lai, M.-D. Solubility and Diffusivity of N_2O and CO_2 in (Monoethanolamine + *N*-methyldiethanoloamine + Water) and in (Monoethanolamine + 2-Amino-2-methyl-1-propanol + water). *J. Chem. Eng. Data* **1995**, 40, 486-492.

(21) Hagewiesche, D. P.; Ashour, S. S.; Sandall, O. C. Solubility and Diffusivity of Nitrous Oxide in Ternary Mixtures of Water, Monoethanolamine, and *N*-methyldiethanolamine and Solution Densities and Viscosities. *J. Chem. Eng. Data* **1995**, 40, 627-629.

(22) Wang, Y. W.; Xu, S.; Otto, F. D.; Mather, A. E. Solubility of N_2O in Alkanolamines and in Mixed Amines. *Chem. Eng. J.* **1992**, 48, 31-40.

(23) Derks, P. W.; Hogendoorn, K. J.; Versteeg, G. F. Solubility of N_2O in and Density, Viscosity, and Surface Tension of Aqueous Piperazine Solutions. *J. Chem. Eng. Data* **2005**, 50, 1947-1950.

(24) Kent, R. L.; Eisenberg, B. Better Data for Amine Treating. *Hydrocarbon Process.* **1976**, 55, 97.

(25) Iliuta, M.; Larachi, F.; Grandjean, B. P. A. Solubility of Hydrogen Sulfide in Aqueous Solutions of Fe(II) Complexes of *Trans*-1,2-cyclohexanediaminetetraacetic Acid. *Fluid Phase Equilib.* **2004**, 218, 305-313.

(26) Iliuta, M.; Larachi, F. Solubility of Oxygen in Aqueous Solutions of Fe(III) Complexes of *Trans*-1,2-cyclohexanediaminetetraacetic Acid (CDTA) as a Function of Temperature and Chelate Concentration. *J. Chem. Eng. Data* **2004**, 49, 1691-1696.

(27) Park, S. H.; Lee, K. B.; Hyun, J. C.; Kim, S. H. Correlation and Prediction of the Solubility of Carbon Dioxide in Aqueous Alkanolamine and Mixed Alkanolamine Solutions. *Ind. Eng. Chem. Res.* **2002**, 41, 1658-1665.

(28) Li, M.-H.; Chang, B.-C. Solubilities of Carbon Dioxide in Water + Monoethanolamine + 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1994**, 39, 448-452.

(29) Li, M.-H.; Shen, K.-P. Calculation of Equilibrium Solubility of Carbon Dioxide in Aqueous Mixtures of Monoethanolamine with Methyldiethanolamine. *Fluid Phase Equilib.* **1993**, 85, 129-140.

(30) Tontiwachwuthikul, P.; Melsen, A.; Lim, C. J. Solubility of CO_2 in 2-Amino-2-methyl-1-propanol Solutions. *J. Chem. Eng. Data* **1991**, 36, 130-133.

(31) Deshmukh, R. D.; Mather, A. E. A Mathematical Model for Equilibrium Solubility of Hydrogen Sulphide and Carbon Dioxide in Aqueous Alkanolamine Solutions. *Chem. Eng. Sci.* **1981**, 36, 355-362.

(32) Al-Ghawas, H A.; Hagewiesche, D. P.; Ruiz-Ibanez, G.; Sandall, O. C. Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine. *J. Chem. Eng. Data* **1989**, 34, 385-391.

CONCLUSION

In this work, aqueous 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), a primary sterically hindered amine, was studied as potential carbon dioxide capture solutions for an enzymatic process relying on type II human carbonic anhydrase. The solubility of CO_2 in aqueous AHPD solutions was measured for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) mass % at (283.15, 298.15 and 313.15) K and for CO_2 partial pressures ranging from (2 to 75) kPa. The experimental conditions were chosen in direct industrial connections (CO_2 Solution Inc.). It was found that the solubility of CO_2 increases with increasing AHPD concentration, increasing CO_2 partial pressures and decreasing temperature.

The modified Kent-Eisenberg model was used to correlate the equilibrium solubility of carbon dioxide in aqueous AHPD solutions and to determine the deprotonation constant K_a and carbamate stability constant K_c for AHPD solutions. The chemical equilibrium constants are expressed as functions of temperature, amine concentration (m in mol/L) and carbon dioxide loading (α). There was a good agreement between the experimental results and those calculated from the equilibrium model. Indeed, the absolute average deviation (AAD) between calculated and experimental results is only of 1.55 % whereas the deviations between the calculated and experimental results were between (0.0164 to 7.07) %. This confirms the adequacy of the Kent and Eisenberg variant model used here to fit the CO_2 solubility data in dilute AHPD aqueous solutions with and without free type II human carbonic anhydrase.

The solubility of N_2O in aqueous AHPD solutions was measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K and was used to estimate the physical solubility of CO_2 in aqueous AHPD solutions. The results are expressed in terms of Henry's law constants. The physical solubility of CO_2 was found to decrease with increasing AHPD concentration and increasing temperature.

The influence of the presence of enzyme on the solubility of CO_2 in an aqueous solution of 2.5 mass % AHPD at (283.15, 298.15 and 313.15) K was also studied for CO_2 partial pressures below 9 kPa. It was found that the enzyme does not seem to influence the solubility of CO_2 in these solutions as the enzyme's function is to catalyze the hydration of

CO_2 without changing in any meaningful manner the CO_2 solubility as dictated by thermodynamics.

The densities and viscosities of aqueous AHPD solutions were measured for AHPD mass fractions of (0.15, 0.5, 1, 2.5 and 10) % at (283.15, 298.15 and 313.15) K and for an aqueous solution of AHPD mass fraction of 2.5 % with an enzyme concentration of 500 mg/L at (283.15, 298.15 and 313.15) K. The density of aqueous AHPD solutions were also measured at (288.15, 293.15, 303.15 and 308.15) K. It was found that the densities and viscosities of aqueous AHPD solutions increasing with increasing AHPD concentration and decreasing temperature. An enzyme concentration of 500 mg/L doesn't seem to affect the density and viscosity of an aqueous AHPD solution of AHPD mass fraction of 2.5 %.

The new experimental data and thermodynamic model developed in this work are useful in the case where AHPD is used in an enzymatic CO_2 capture process. The experimental conditions studied in this work are compatible with industrial conditions typically encountered. The function of AHPD in these processes consists to enhance the solubility of CO_2 in the aqueous solutions and also to slow down the pH decrease in the solutions since the pH is a key parameter for maintenance of an optimal enzyme activity. The thermodynamic model is also useful to predict the equilibrium solubility of CO_2 in aqueous AHPD solutions for intermediate experimental conditions.

Some additional work could be performed to check the solubility of CO_2 in other aqueous sterically hindered amine solutions like AMP, AMPD and AEPD for the same experimental conditions. The experimental conditions could also be modified to provide the solubility of CO_2 in aqueous amine solutions for a wide range of temperature, amine mass fractions in the solutions and partial pressures of CO_2.

APPENDIX A. Figure of the experimental system
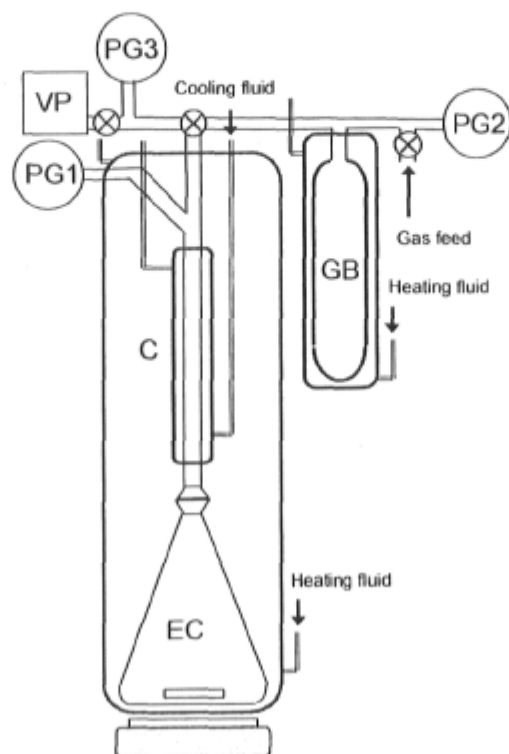
Figure A.1. Solubility apparatus. EC, equilibrium cell; GB, gas buret; C, condenser; PG1 and PG2, precision pressure gauges; PG3, vacuum gauge; VP, vacuum pump.

APPENDIX B. Estimated physical concentrations of CO_2/total concentrations of CO_2

Table B.1. Fractions of estimated physical concentrations of CO_2 $\left(C_{CO_2 phys.}\right)$/total concentrations of CO_2 (%) in the aqueous AHPD solutions for AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % at 283.15 K

283.15 K							
0.15 %		0.5 %		1 %		2.5 %	
P_{CO_2}	$C_{CO_2 phys.}/C_{CO_2}$ (%)	P_{CO_2}	$C_{CO_2 phys.}/C_{CO_2}$ (%)	P_{CO_2}	$C_{CO_2 phys.}/C_{CO_2}$ (%)	P_{CO_2}	$C_{CO_2 phys.}/C_{CO_2}$ (%)
3.19	12.4	4.25	5.68	3.65	2.78	2.98	1.13
5.35	18.9	10.1	12.0	9.18	6.15	7.29	2.26
12.0	33.7	22.3	22.8	15.7	9.77	15.4	4.26
25.9	52.0	44.8	37.4	23.1	13.6	27.7	7,20
43.2	65.4	67.7	48.0	47.7	24.2	49.3	11,8
61.9	74.5	68.7	48.1	74.1	33.6	69.7	16.0
64.0	73.8						
68.8	75.9						

APPENDIX C. Experimental results
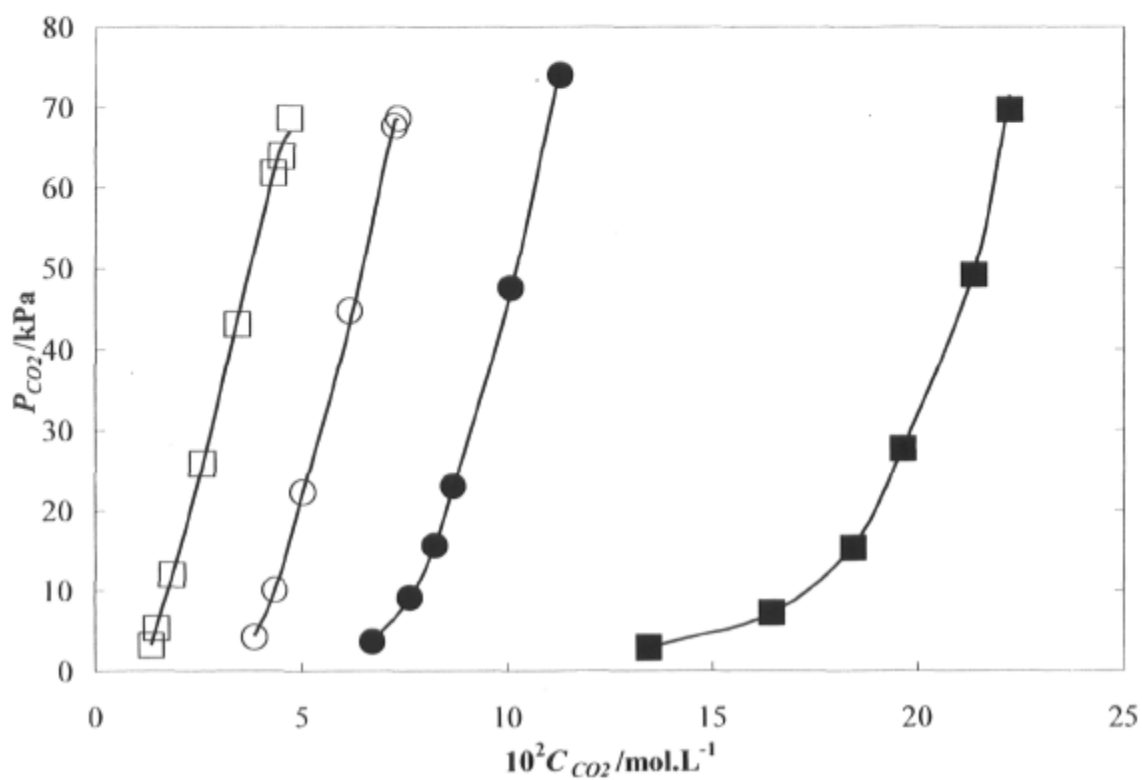
Figure C.1. Solubilities of carbon dioxide in aqueous AHPD mass fractions of (0.15, 0.5, 1 and 2.5) % solutions at 283.15 K: □, 0.15; ○, 0.5; ●, 1; ■, 2.5. Lines calculated by the thermodynamic model.
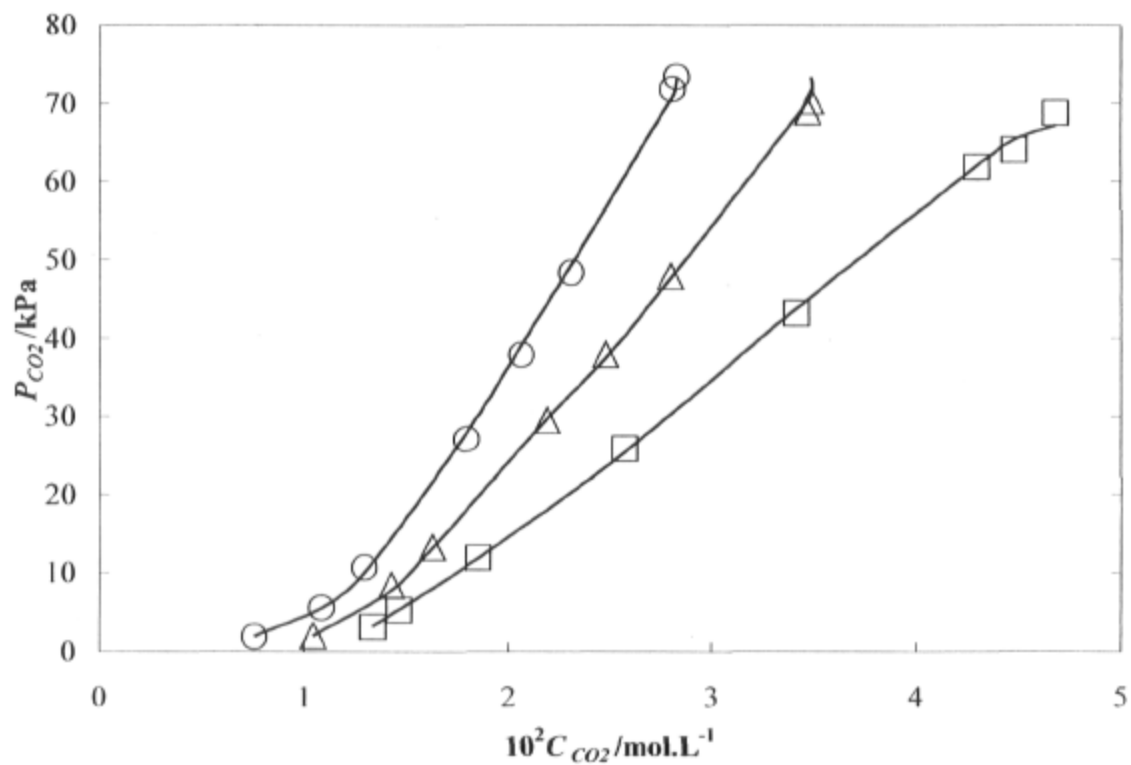
Figure C.2. Solubilities of carbon dioxide in an aqueous AHPD mass fraction of 0.15 % solution at various temperatures: □, 283.15 K; Δ, 298.15 K; ○, 313.15 K. Lines calculated by the thermodynamic model.

APPENDIX D. Numerical values of K_a and K_c

Table D.1. Numerical Values of K_a (mol/L) and K_c (L/mol) in Function of Temperature (in K), CO_2 Loading (α) and Initial Amine Concentration (m) Ranging from (12 to 207) mmol/L (AHPD Mass Fractions Ranging from (0.15 to 2.5) %)

283.15 K

12 mmol/L (0.15 %)			41 mmol/L (0.5 %)			83 mmol/L (1 %)			207 mmol/L (2.5 %)		
α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c
1.07 (1.33)	$7.80 \cdot 10^{-12}$	$2.96 \cdot 10^{-3}$	0.928 (3.84)	$1,78 \cdot 10^{-12}$	$1,40 \cdot 10^{-2}$	0.811 (6.72)	$3.58 \cdot 10^{-13}$	$3.82 \cdot 10^{-2}$	0.647 (13.44)	$1.16 \cdot 10^{-14}$	$1.49 \cdot 10^{-1}$
1.17 (1.46)	$1.79 \cdot 10^{-11}$	$2.36 \cdot 10^{-3}$	1.05 (4.33)	$6,33 \cdot 10^{-12}$	$1,04 \cdot 10^{-2}$	0.924 (7.65)	$1.74 \cdot 10^{-12}$	$2.80 \cdot 10^{-2}$	0.796 (16.45)	$2.86 \cdot 10^{-13}$	$9.82 \cdot 10^{-2}$
1.49 (1.85)	$1.29 \cdot 10^{-10}$	$1.27 \cdot 10^{-3}$	1.21 (5.02)	$2,51 \cdot 10^{-11}$	$7,08 \cdot 10^{-3}$	0.998 (8.24)	$4.00 \cdot 10^{-12}$	$2.31 \cdot 10^{-2}$	0.888 (18.44)	$1.14 \cdot 10^{-12}$	$7.63 \cdot 10^{-2}$
2.07 (2.58)	$1.56 \cdot 10^{-9}$	$5.32 \cdot 10^{-4}$	1.49 (6.15)	$1,33 \cdot 10^{-10}$	$4,18 \cdot 10^{-3}$	1.05 (8.69)	$6.67 \cdot 10^{-12}$	$2.04 \cdot 10^{-2}$	0.948 (19.65)	$2.38 \cdot 10^{-12}$	$6.50 \cdot 10^{-2}$
2.75 (3.42)	$1.37 \cdot 10^{-8}$	$2.47 \cdot 10^{-4}$	1.76 (7.25)	$4,71 \cdot 10^{-10}$	$2,69 \cdot 10^{-3}$	1.22 (10.09)	$2.69 \cdot 10^{-11}$	$1.38 \cdot 10^{-2}$	.,03 (21.39)	$5.68 \cdot 10^{-12}$	$5.30 \cdot 10^{-2}$
3.47 (4.30)	$1.01 \cdot 10^{-7}$	$1.26 \cdot 10^{-4}$	1.78 (7.34)	$5,13 \cdot 10^{-10}$	$2,62 \cdot 10^{-3}$	1.36 (11.29)	$6.77 \cdot 10^{-11}$	$1.04 \cdot 10^{-2}$	1.07 (22.26)	$8.26 \cdot 10^{-12}$	$4.81 \cdot 10^{-2}$
3.61 (4.48)	$1.47 \cdot 10^{-7}$	$1.11 \cdot 10^{-4}$									
3.78 (4.68)	$2.29 \cdot 10^{-7}$	$9.60 \cdot 10^{-5}$									

298.15 K

12 mmol/L (0.15 %)			41 mmol/L (0.5 %)			83 mmol/L (1 %)			207 mmol/L (2.5 %)		
α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c	α $(10^2 C_{CO_2}{}^a)$	K_a	K_c
0.843 (1.04)	$1.49 \cdot 10^{-12}$	$1.89 \cdot 10^{-3}$	0.753 (3.11)	$3.38 \cdot 10^{-13}$	$7.99 \cdot 10^{-3}$	0.609 (5.03)	$9.91 \cdot 10^{-15}$	$2.33 \cdot 10^{-2}$	0.446 (9.25)	$4.46 \cdot 10^{-18}$	$6.57 \cdot 10^{-2}$
1.15 (1.43)	$3.98 \cdot 10^{-11}$	$8.78 \cdot 10^{-4}$	0.848 (3.50)	$1.66 \cdot 10^{-12}$	$6.11 \cdot 10^{-3}$	0.674 (5.57)	$6.25 \cdot 10^{-14}$	$1.97 \cdot 10^{-2}$	0.605 (12.53)	$9.00 \cdot 10^{-15}$	$5.82 \cdot 10^{-2}$
1.31	$1.27 \cdot$	$6.19 \cdot$	0.926	$4.68 \cdot$	$4.95 \cdot$	0.733	$2.32 \cdot$	$1.67 \cdot$	0.697	$1.10 \cdot$	$4.59 \cdot$

α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c
(1.62)	10^{-10}	10^{-4}	(3.82)	10^{-12}	10^{-3}	(6.04)	10^{-13}	10^{-2}	(14.43)	10^{-13}	10^{-2}
1.77 (2.19)	$1.30\cdot10^{-9}$	$2.84\cdot10^{-4}$	1.10 (4.55)	$2.80\cdot10^{-11}$	$3.20\cdot10^{-3}$	0.761 (6.26)	$4.06\cdot10^{-13}$	$1.54\cdot10^{-2}$	0.801 (16.59)	$8.51\cdot10^{-13}$	$3.41\cdot10^{-2}$
2.01 (2.48)	$3.27\cdot10^{-9}$	$2.04\cdot10^{-4}$	1.30 (5.35)	$1.19\cdot10^{-10}$	$2.10\cdot10^{-3}$	0.850 (7.02)	$1.76\cdot10^{-12}$	$1.20\cdot10^{-2}$	0.931 (19.24)	$5.26\cdot10^{-12}$	$2.39\cdot10^{-2}$
2.27 (2.80)	$8.14\cdot10^{-9}$	$1.48\cdot10^{-4}$	1.49 (6.16)	$3.68\cdot10^{-10}$	$1.46\cdot10^{-3}$	0.929 (7.67)	$5.01\cdot10^{-12}$	$9.72\cdot10^{-3}$	0.963 (19.94)	$7.61\cdot10^{-12}$	$2.21\cdot10^{-2}$
2.78 (3.47)	$3.99\cdot10^{-8}$	$8.55\cdot10^{-5}$				1.10 (9.05)	$2.75\cdot10^{-11}$	$6.41\cdot10^{-3}$			
2.81 (3.49)	$4.47\cdot10^{-8}$	$8.15\cdot10^{-5}$				1.19 (9.85)	$5.78\cdot10^{-11}$	$5.21\cdot10^{-3}$			

313.15 K

12 mmol/L (0.15 %)			41 mmol/L (0.5 %)			83 mmol/L (1 %)			207 mmol/L (2.5 %)		
α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c	α ($10^2 C_{CO_2}{}^a$)	K_a	K_c
0.612 (0.75)	$2.78\cdot10^{-14}$	$1.70\cdot10^{-3}$	0.470 (1.93)	$5.63\cdot10^{-17}$	$6.58\cdot10^{-3}$	0.354 (2.91)	$1.57\cdot10^{-21}$	$7.03\cdot10^{-3}$	0.317 (6.54)	$5.45\cdot10^{-24}$	$9.20\cdot10^{-3}$
0.878 (1.08)	$6.69\cdot10^{-12}$	$8.20\cdot10^{-4}$	0.627 (2.57)	$4.62\cdot10^{-14}$	$5.36\cdot10^{-3}$	0.526 (4.32)	$1.11\cdot10^{-15}$	$1.29\cdot10^{-2}$	0.356 (7.34)	$2.12\cdot10^{-21}$	$1.79\cdot10^{-2}$
1.05 (1.29)	$4.60\cdot10^{-11}$	$5.27\cdot10^{-4}$	0.775 (3.18)	$1.39\cdot10^{-12}$	$3.58\cdot10^{-3}$	0.667 (5.47)	$1.44\cdot10^{-13}$	$9.55\cdot10^{-3}$	0.411 (8.48)	$7.55\cdot10^{-19}$	$2.79\cdot10^{-2}$
1.45 (1.79)	$7.75\cdot10^{-10}$	$2.29\cdot10^{-4}$	0.964 (3.956)	$2.00\cdot10^{-11}$	$2.13\cdot10^{-3}$	0.770 (6.33)	$1.31\cdot10^{-12}$	$7.19\cdot10^{-3}$	0.532 (10.97)	$1.56\cdot10^{-15}$	$3.17\cdot10^{-2}$
1.68 (2.06)	$2.37\cdot10^{-9}$	$1.56\cdot10^{-4}$	1,14 (4.69)	$1.07\cdot10^{-10}$	$1.39\cdot10^{-3}$	0.949 (7.80)	$1.72\cdot10^{-11}$	$4.41\cdot10^{-3}$	0.680 (13.97)	$2.02\cdot10^{-13}$	$2.28\cdot10^{-2}$
1.88 (2.31)	$5.45\cdot10^{-9}$	$1.16\cdot10^{-4}$	1,29 (5.29)	$3.09\cdot10^{-10}$	$1.02\cdot10^{-3}$	1,03 (8.49)	$4.20\cdot10^{-11}$	$3.56\cdot10^{-3}$	0.787 (16.08)	$1.82\cdot10^{-12}$	$1.68\cdot10^{-2}$
2.27 (2.81)	$2.30\cdot10^{-8}$	$6.99\cdot10^{-5}$							0.836 (16.85)	$4.01\cdot10^{-12}$	$1.45\cdot10^{-2}$
2.30 (2.83)	$2.50\cdot10^{-8}$	$6.76\cdot10^{-5}$									

$^a C_{CO_2} = \left[RNHCOO^- \right] + \left[CO_2 \right] + \left[HCO_3^- \right] + \left[CO_3^{2-} \right]$ expressed in $mol \cdot L^{-1}$